A COMPARISON OF THE POLLUTION RECORD OF SOUTH MERSEYSIDE FROM SEDIMENT CORES TAKEN FROM THE ESTUARY AND A SMALL LAKE

Thesis submitted in accordance with the requirements of the University of Liverpool for the degree of Doctor in Philosophy

by

Mary-Jo Hoare

June 2012

Abstract

The ability to assess the contamination of sediments in estuaries and lakes is extremely important. This is because of various factors, both natural (tidal action, chemical remobilisation) and anthropogenic (e.g. building work), that lead to the disturbance of the sediment can result in the remobilisation or resuspension of the pollutants and, if high levels of pollutants are present in a region, they can be responsible for a number of health impacts on the local population. The use of sediment cores to investigate the pollution levels in the sediment is a relatively easy method of assessing contamination.

The main aims of this study were to investigate pollution in saltmarsh, intertidal and lake sediment cores taken from the South Liverpool area and to attempt to distinguish different pollutant transport pathways between cores.

This was done using sediment cores taken from a saltmarsh, intertidal area and lake in South Merseyside and measuring the heavy metal and persistent organic pollutant (PAH and PCB) content using a variety of methods including; X-Ray Fluorescence, Environmental Magnetism, Gas Chromatography/Mass Spectrometry and Flame Atomic Absorption Spectrometry.

The results showed that, although the pollution input to the region has reduced over the last 30 years, there are still high levels of certain chemicals (including lead, mercury and PCBs) in the environment. The concentrations of the main pollutants (Pb, Zn, Hg, Cd, PCBs and PAHs) are above guideline levels that are considered dangerous to aquatic organisms, however with the exception of Cd at Speke, none of the metals are present at a concentration that would be considered dangerous to human health. The main source of pollution to the saltmarsh is aquatic, whilst the main input to the lake core is from atmospheric deposition.

From the data acquired for this project it would appear that the core from the Speke Hall Lake location provides a more accurate record of the pollution history of the area than those from the more dynamic saltmarsh environment.

Acknowledgements

I would like to thank my supervisors, Professor Andy Plater and Professor George Wolff, for all their help, support, guidance and patience during this project.

I would also like to thank Dr Alex Stewart from the Health Protection Authority for his invaluable help with accessing the renal and heart disease data, Dr Anu Thompson for all her assistance with the organic geochemistry part of the project, Mrs Irene Cooper for her help with the AA and particle size analysis (and for providing redbush tea when needed), Mr Bob Jude for his help with the magnetics and XRF work, Mr Alan Henderson for assistance with LOI, Hg and Cd extractions, Miss Sabena Blackbird for her help with the TOC analysis, Dr John Boyle for his help with the XRF data and Mr Antonio Da Cruz for his help with the GIS maps.

Other people I would like to thank for their assistance during my time at Liverpool include Mrs Paula Houghton and Mrs Hilda Hull for their help with ordering equipment and reagents, Carmel Pinnington, Dr Liz Fisher, Mr Ian Ford (warden at Speke Hall) and Mr Malcolm Verity and Mr Roy Forshaw for their help with the industrial history of the region and Dr Marta (Garcia-Finana) Van der Hoek for her advice regarding the statistical analysis.

Finally I would like to thank my family for their patience and support during this project.

CONTENTS

CHAPTER 7

SPEKE HALL LAKE RESULTS

CHAPTER 8

UPPER MARSH CORE DISCUSSION

List of Figures

List of tables

Correlation Tables Appendix 1

CHAPTER 1

A COMPARISON OF THE POLLUTION RECORD OF SOUTH MERSEYSIDE FROM SEDIMENT CORES TAKEN FROM THE ESTUARY AND A SMALL LAKE

1.1. Introduction and Overview of the Project

The ability to assess the contamination of sediments in estuaries and lakes is extremely important. This is because of various factors, both natural (tidal action, chemical remobilisation) and anthropogenic (e.g. building work), that lead to the disturbance of the sediment can result in the remobilisation or resuspension of the pollutants (Forstner and Muller, 1981). These can then, potentially, enter the food chain or result in direct human exposure to contaminants *via* leisure activities such as swimming, boating and fishing.

A proportion of the pollutants entering the estuarine and lacustrine environment adsorb onto sediment particles which eventually settle out and are incorporated into the sediment record (Forstner and Muller, 1981). It may be possible to use these sediments to identify areas and periods of time where the population has been exposed to chronic long-term pollution and hence identify the likely causes of current patterns of health impacts and potential future health problems in south Liverpool.

It has been shown that people living near contaminated land sites are likely to suffer from higher incidence of certain diseases. For example, Staples *et al.* (2003) have shown how exposure to hexachlorobutadiene (HCBD – a by-product of the manufacture of chlorinated hydrocarbons) influences the occurrence of renal disease in those living near a source of the chemical (the toxic effects improved in those subjects who moved away from the location). A study in Sweden has shown higher incidence of end stage renal disease in proximity to a cadmium emitting battery plant (Hellström, 2001). Numerous studies have shown a link between chemical release to the environment and cancer in exposed populations (Friberg *et al.*, 1986[b]; Fischer,

1987; Kazantzis, 1987; Heinrich, 1988; Chen *et al.,* 1992, Chiou *et al.,* 1995; Klein, 1996).

1.2. Aims and Hypotheses

The aims of this study are:

1. To investigate historic pollution in saltmarsh, intertidal and lake sediment cores taken from the South Liverpool area.

2. To attempt to distinguish different pollutant transport pathways between cores from a lake and the intertidal zone.

3. To assess (as a discussion point) the potential viability of using the historical pollution record from sediment cores as a method of identifying and explaining pollution-related health issues in local populations.

We considered the following hypotheses:

1. The Mersey Estuary is a historically polluted ecosystem and, although levels of pollution have improved in recent years, pollutants such as heavy metals, Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) are still present in concentrations that are considered to pose potential health problems for aquatic organisms and the local human population.

2. There is a difference in the sources and transport pathways of pollutants reaching sediment cores from different environments (lake and intertidal flat). The lake core is likely to receive most of its pollutants via atmospheric sources, whilst the intertidal zone will receive predominantly aqueous pollution

3. The ability to use a sediment core as a method of identifying historical pollution inputs to a region will be dependent on the level of disturbance at a site and the pathways the pollutants take to reach the sediment.

4. The ability to use historic records of pollutant input to a region as a method to explain disease incidence is dependent on various factors including; local population dynamics, the continuity of the pollution record and the level of detail available in the health records available for a region.

1.3 Thesis Structure

The following study is divided into a number of chapters. Chapters 1, 2 and 3 expand on the research aims and background to the study, detailing previous work done in the area, the processes operating in the different environments and the land-use and pollution history of the region. Chapter 4 is a description of the methods used to collect data for the study. Chapters 5, 6 and 7 are a description of the results of the study, whilst chapters 8, 9, 10 are a discussion of the results for the individual cores. Chapter 11 looks at the differences between the cores from different environments in the same geographic area and suggests reasons for these differences. Chapter 12 draws conclusions from the data presented and suggests further avenues of research that could be pursued. The final sections of the thesis are the appendices (including correlation matrices and a brief overview of selected health data from the region) and the list of references used in the text.

1.4 The Liverpool Bay and Mersey Basin Study Area

Although the cores examined are from the South Liverpool area and therefore will most likely reflect localised pollution input, it is possible that some of the pollution will be from longer range transport processes including riverine and atmospheric, so potential sources from the wider Mersey Basin area are considered here.

Any study looking at the Mersey Basin must take into consideration the influence of factors in the Liverpool Bay area (Figure 1). This is an area that covers three counties (Lancashire, Merseyside and Cheshire) and stretches from Rossall Point, Fleetwood (Lancashire) in the north, to the Welsh border of the Dee Estuary in the south. It

includes the estuaries of the Dee, Mersey, Alt and Ribble and a range of coastal habitats such as saltmarshes, sand dunes and soft cliffs (George, 1997).

Figure 1: Liverpool Bay.

The Mersey Basin catchment (Figure 2) is located on the northwest coast of England. It encompasses St Helens and Stalybridge in the north and north east, the Pennine fringe (between Manchester and the Pennines in the east and Stockport and Ellesmere Port in the South (Tomlinson, 1997) and includes most of the catchments of the Rivers Mersey and Irwell.

1.5 Previous Research into Pollution in the Region

Due to the industrial history of the Mersey Basin region there has been a wide variety of research done on metal and organic pollution in the Mersey Basin. The following section presents a review of that research. Although there is a high degree of overlap in the research, an attempt has been made here to consider work undertaken in the river, in the estuary, then the Liverpool Bay area and finally work done in a number of small lakes in the region.

Pollution levels in the Mersey increased from around the 1850s until more stringent discharge regulations began to be introduced in the 1970s. The main sources of

heavy metals in the estuary at present are bed sediments, sea water, domestic discharges and river discharges (Hartnett and Berry, 2010). In general, levels of all heavy metals in Mersey sediments have been declining in recent years, although they are still enhanced when compared to unpolluted sediments. Decreases are, as mentioned above, probably related to stricter discharge regulations, a decline in industry in the region and improved efficiency in manufacturing processes (Harland *et al.*, 2000).

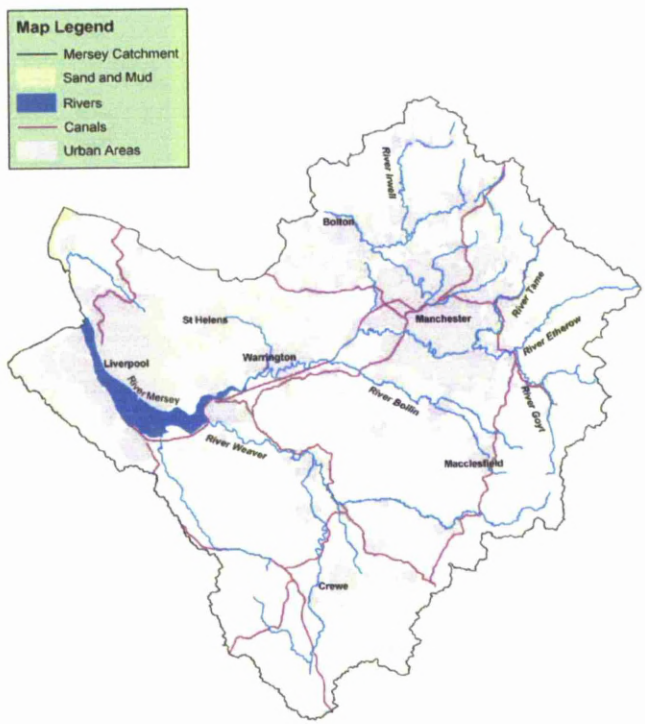


Figure 2: The Mersey Catchment (taken from the Mersey Basin Campaign leaflet – 'Mersey 6 minute expert'.

Turner *et al.* (2004) found that around 30% of dissolved Cd in river water from the Mersey was associated with hydrophobic organic matter, but this decreased with increasing salinity. The opposite situation was found with Zn concentration which increased from 40% in river water to 90% associated with hydrophobic organic matter in seawater. Around 80-90% of Hg was associated with hydrophobic organic matter and this appeared to be unaffected by salinity. They also showed that particulate organic matter and the presence of oxides were important for Cd partitioning within the estuary and that the absence of oxides is important for the salting out of Hg, possibly due to a greater abundance of sorption sites in their

absence. Ni appeared to exhibit characteristics of both Hg and Cd. They also suggested that the presence of silicates, particulate organic matter (POM) and salinity are important factors controlling metal behaviour

A study by Ridgeway *et al.* (2003) showed enhanced levels of industrial pollution indicator metals Zn, Sn and Pb (and slightly raised levels of As and Cu) in the Mersey and its tributaries (Irwell, Weaver). Upstream (between Stockport and Sale, in an area were the drainage basin encompasses a large part of industrialised Manchester) there were higher levels of As, Sn and Pb. In the lower Mersey Basin area concentrations of P, Zn, As, Sn and Pb were all raised, as were Sr and Ca (probably due to the presence of the shells of marine organisms). Cr, Rb and Zr were also present in elevated concentrations. The authors suggest that there is a considerable amount of P, Ti, Fe, V, Cr, Ni, Cu, Zn, As, Y, Zr, Nb, Sn, Ba and Pb being stored upstream in the catchment (possibly in the Manchester Ship Canal) and these are being diluted by cleaner sediments entering form the seaward end of the estuary. They suggest that the major contaminant is Zn, but overall levels of contamination in the Mersey have decreased in recent years.

Martino *et al.* (2002) investigated metals in sediments and water from the Mersey Estuary. They found a correlation between dissolved Co and Ni, suggesting a common source for these metals that was different to that of Zn and Pb. They found enrichment of Cd, Co, Cu, Ni and Pb in bed sediments compared to suspended particulate matter and suggested that one of the main sources for metals in the estuary is resuspension of contaminated sediments. They also discussed the possibility that constant resuspension of sediment limits the amount of early diagenesis occurring. This is because the mixing process limits the development of anoxic conditions in the surface sediments and in areas where mixing is occurring it might limit the availability of the metals to the water column. Another source of metals could be desorption from suspended particulate matter and, although they found little evidence of this in the more saline parts of the estuary, there does seem to be the possibility of desorption from bed sediments in brackish and freshwater areas, and areas where the concentration of metals in the sediment porewater is greater than that in the water column.

A study by Comber *et al.* (1995) found that in the Mersey at the freshwater/saline interface and in lower salinity areas Cd, Cr, Cu and Zn are removed from sediments. They found a decrease in dissolved Zn compared to a previous study which suggesting that programme of reduced sewage inputs was having a positive effect on lowering the levels of metal pollution in the estuary.

Langston (1986) found that sediment from the Mersey was at least moderately contaminated with all metals investigated and in some cases (mainly at upstream sites) high levels of contamination (Cd, Mn Ni) were found, Hg was consistently found at high concentrations throughout the estuary and correlated well with sedimentary organic matter concentration. A number of mid estuarine peaks for Sn, Cr, Cu and Ni suggested specific point sources for these metals. During the period of the study (4 years) Pb and Hg contamination in biota and Hg in sediment decreased by half, indicating that clean up procedures for these metals were beginning to take effect.

Turner (2000) investigated the link between Fe and Mn oxyhydroxides and pollutant metals in a number of UK estuaries including the Mersey. These Fe/Mn oxides are particularly important because metals attached to these oxides are potentially bioavailable to burrowing organisms when ingested or are released to porewater during early diagenesis. It was concluded that Fe is the most important oxide for metal binding and that metal association with Mn is not just controlled by Mn concentrations. The strong tidal currents in the Mersey appear to provide a buffer to localised pollution sources (human and diagenetic) by dispersing the fine grained sediment (which metals preferentially bind to) over a wide area. Strong correlations were found between Zn and Pb, probably because these are fairly common industrial pollutant metals. Turner (2000) suggested that estuaries trap Zn more efficiently than Pb due to differences in affinity for particle sizes, diagenesis and possible environmental sources and transport pathways. The Mersey seems to have significant Cr contamination but only moderately raised Cu levels, probably due to variations in sources and differences in geochemical behaviour. Cu preferentially associates with organic matter rather than Fe/Mn oxides. Correlations between Fe/Mn and contaminant metals suggest that those metals tend to sorb to or coprecipitate out with

the Fe/Mn oxides, whilst correlations between contaminant metals themselves suggests a common source or dispersal pattern.

Laboratory experiments studying the behaviour of Cu, Zn, Fe and Mn in sediments from the Mersey showed that with temperature increases the amount of Cu, Mn and Zn in the dissolved phase increased but salinity variations had little effect. pH and Oxygen variations appeared to have little effect on Cu and Zn. However, Fe and Mn release on oxidation is suppressed by increasing pH. Low oxygen resulted in slow but significant releases of Fe. Overall, it was concluded that due to the scavenging by resuspended sediment of metals from the water column, the resuspension and oxidation of anoxic sediments would not be a major contributing factor to metal pollution (Hirst and Aston, 1983)

Hartnett and Berry (2010) found that concentrations of Pb in the sediments decreased from Howley Weir towards the Irish Sea and this seemed to be related to an increase in salinity. This finding supported work done by Charlesworth *et al.* (2006) and suggests a link with freshwater input to the estuary. However, there is also some Pb input from atmospheric sources (Charlesworth *et al.*, 2006).

Vane *et al.* (2009) found Hg levels in Mersey sediment varied depending on the sampling location with the highest concentrations being found in the Hale and Ince Banks part of the estuary, partially due to the relatively higher concentrations of fine grained muds in these areas (Hale is close to Oglet Bay). The amount of coarse grained material increased towards the outer estuary but decreases in Hg could also be related to dilution by less contaminated material from the Irish Sea and increasing distance from the major discharge points (Manchester Ship Canal). Hg concentrations were also found to be higher in sediment collected from the edge of the estuary, rather than from the middle and all correlated well with LOI (Loss on Ignition), The concentrations of Hg recorded at the Weaver Sluice and Eastham docks were lower than previous studies conducted in that region (Langston, 1986) and indicated a decline in the Hg discharges to the Mersey in recent years (Vane *et al.*, 2009).

Mercury in the Mersey correlates well with the silt grain size fraction and has shown an overall decrease since 1974. Although between 1987 and 1992 there was an increase in concentration, possibly due to remobilised Hg entering the environment from eroding saltmarshes at Ince and Stanlow (Harland *et al.*, 2000).

Bartlett and Graig (1981) showed higher levels of Hg contamination in shoreline sites than in sites out in the estuary and a correlation between organic carbon and total Hg concentration and Hg and the silt sediment fraction (probably due to Hg binding to sulphur in the organic matter and ion exchange sites on the silt). They also found that the redox potential and bacteria activity of the sediment were important in methyl mercury contamination levels – in more aerobic sediments sulphide concentrations are higher and so are methyl mercury concentrations. Rae and Aston (1981) made similar findings for Hg, organic matter and grain size correlations, as did Airey and Jones (1982).

Martino *et al.* (2004) found high levels of Ni in river water from the Mersey as compared to other rivers in less industrialised areas, with concentrations being lower near the Liverpool Bay end of the estuary. They showed that at the Howley Weir end of the estuary the concentration of Ni in the water was inversely related to flow, suggesting that higher flow dilutes the Ni concentration. They also showed that there was reduced lability of Ni in summer, possibly due to increased residence time allowing the formation of more stable complexes or due to different sources of Ni in summer. They suggest that at present the major source of Ni in the estuary is no longer from pollutant input, but from resuspension and redistribution of historically contaminated sediments.

Campbell *et al.* (1988) suggested that Ni contamination was primarily related to industrial discharge, whilst Zn is influenced by sewage input and by remobilisation of Zn from disturbed sediments.

High background levels of Al in Mersey sediment could be due to the presence of Al containing feldspar (Harland *et al.*, 2000).

Levels of PCBs and DDT (Dichlorodiphenyltrichloroethane) contamination in the Mersey have been decreasing over the last 50 years (Fox *et al.*, 2001). Using sediment cores taken from stable saltmarshes in the region they showed the start date of DDT pollution matched well between sample sites, as did the peak concentrations found in the cores. They found PCB contamination in Mersey sediments started around 1940 and peaked in the 1970s, after which concentrations in sediment started to decrease. Although levels were still high, probably due to the persistence of PCBs and their continued release to the environment, e.g. from old electrical equipment. HCH distribution was found to vary considerably between cores and only low levels of dieldrin were found. HCB exhibited a complex profile in the sediments probably due to its wide variety of sources including pesticides and as a by-product of manufacturing processes. In this study there did not seem to be any relationship between particle size or organic matter and the pollutants (Fox *et al.*, 2001).

A study by Fox *et al.* (1999) used pollution (DDT and heavy metals) as a partial method of dating sediments (along with radionuclides). They found different historical contamination profiles in the different samples sites. Particle size distribution was fairly consistent down core, so variations in pollutant metals could be concluded to be due to input rather than particle size influences. The core from Widnes Warth showed 4 benchmark years (1. onset of industrialisation in the 19th century; 2. start of DDT production in Trafford Park Manchester in the 1940s; 3. radionuclide events correlated with Sellafield discharges; 4. the onset of Hg cleanup in the mid 1970s). The Ince core only showed evidence of the last 3 events, as it was not deep enough to record the first due to differences in sedimentation rates. The Widnes core indicated that heavy metal contamination was greatest in the Mersey between 1930s and 1970s.

Levels of PAH concentration in Mersey sediments were investigated by Vane *et al.* (2007) and they found higher concentrations associated with muddy sediments than with sandy sediments (including a site at Oglet Bay which had the highest concentrations found – 3766μg/kg). This was partially explained using a correlation with sediment organic matter content (TOC – Total Organic Carbon). PAHs were primarily from high temperature combustion processes, but variation in ratios indicated a range of sources for these compounds, reflecting the wide variety of

industry in the area. This study did not show a significant correlation between PCBs and TOC possibly because of a masking effect caused by localised inputs and geochemical processes. There was however, a suggested grain size control on the PCB sediment concentration with higher levels found in finer grained sediments, but no obvious relationship between sample site location within the estuary and PCB concentrations was found. Mean PCB concentration appeared to be higher for the Mersey than for other estuaries in the UK (e.g. Thames, Clyde and Humber), but lower than other industrialised estuaries in Europe (e.g. Seine and Rhine). Congener distribution indicated a wide variety of sources for the PCBs and overall concentrations increased with core depth. The study also showed that sediments in the estuary have approximately 30 times higher PCB concentrations that those in Liverpool Bay.

Rogers (2002) found concentrations of total PAHs of around 11μg/g from sediment taken at Oglet bay on the Mersey. Other locations had considerably lower concentrations and PAHs showed weak positive correlations with organic matter. They showed that areas near major roads (and in the case of the Mersey, chemical plants) had higher levels of PAHs.

Davies and Wolff (1990) found high levels of hydrocarbon contamination in sediments from the Mersey estuary and these high levels made identifying individual contamination events (like the crude oil spill of Oct 19th, 1989) difficult. Law (1981) found higher concentrations of total hydrocarbons in finer grained sediment from industrialised estuaries (include the Mersey) than in coarse grained sediment from less industrialised areas.

A number of studies have shown that the Mersey is a significant source of pollutants including (Ni, Cu, Zn) to the Irish Sea (Norton *et al.*, 1984; Laslett, 1995; Achterbreg *et al.*, 1996).

A study in 1992 by Camacho-Ibar of Liverpool Bay sediment found Hg to be associated with clays in finer grained sediment but with organic matter in coarser material. Arsenic was associated with Fe/Mn oxyhydroxides. The main source of As seemed to be natural, with a little from sewage sludge disposal, whereas for Hg the

main input was from anthropogenic sources via the river Mersey and some from sewage sludge and dredging.

Camacho-Ibar (1996) found high levels of PCBs particularly associated with the finer grain size fraction (mud) and organic carbon in Liverpool Bay sediments. Organic matter acted as an adsorption site for hydrophobic organic pollutants. It appeared that organic carbon concentration was related to grain size, although due to the large amounts of coarser particles present in Liverpool Bay, these are also an important contributor to the organic carbon and PCB content of the bay. PCB concentrations were lower in the Mersey than some other industrialised estuaries (Hudson and Acushnet), but of similar levels to those found in other open coastal bays (e.g. Humber). PCBs in Liverpool Bay sediments are probably primarily from river input, with some being deposited along with dredged material and some from sewage sludge. Preston and Raymundo (1993) showed a similar relationship between organic carbon, grain size, lipid fraction and linear alkyl benzenes in Mersey estuary sediments.

In a number of papers using Environmental Magnetism and XRF (X-ray Refraction) to look at pollution in lakes in the Merseyside and Cheshire area, Worsley and Power (2009) illustrated a number of different phases of pollution in the region, from the onset of the industrialisation in the 19th century, to its intensification in the 20th century and a gradual decline in pollution with the introduction of the Clean Air Act in the 1950s. These papers also discussed the possibility of using sediment cores as a method of contributing towards the understanding of pollution related health problems in the region (e.g. ARM – Anhysteric Remanent Magnetisation - as a proxy measurement of ultrafine particulates in the atmosphere) (Power *et al.*, 2005; Worsley *et al.*, 2005, 2006; Worsley and Power, 2009;).

1.6 Possible Health Effects of Pollutants

Previous work has established a link between levels of pollutant input to the environment and the health of the population in surrounding areas (Hellström, 2001; Staples *et al.*, 2003).

1.6.1 Organic Pollutants

Due to the significant levels of pollution that humans are exposed to on a daily basis, it can be very difficult to pinpoint the individual effects of particular contaminants or a particular source of contaminants (Lang, 1995; Howard, 1997). This is even more difficult if exposure is to bioaccumulative substances at very low levels (Kortenkamp *et al.*, 2007). It may take several years for the cumulative effects of exposure to show up and, due to the mobility of human populations, it may not be possible to identify many cases of exposure as people move away to other locations.

Much of the research into the effects of organic pollutants on humans has been done at the acute level, e.g. the Japanese rice oil disaster (1968) where PCBs from a heat exchanger at a rice mill severely contaminated rice. Symptoms in the population included dizziness, coughing, abdominal pain, headaches, tiredness, nausea, disturbed vision, discharge from the eyes, damage to the central nervous system, mucous membranes and, in the worst cases, the skin condition chloracne (Masuda, 1985; Bernes, 1998). Many of those affected suffered from long term health problems. Levels in tissue reduced gradually. However, many of the effects in this case can be attributed not to the PCBs but to the fact that the PCBs were, themselves, contaminated with polychlorinated dibenzofurans. The most surprising result from this incident was that there were no acute deaths caused, although the fact that the contaminants have a half-life in tissue of around 5 years meant that long-term exposure problems were considerable and included people exhibiting symptoms 10 years after the spill and a number of deaths from cancers (Masuda, 1985). This supports the need for monitoring of pollutant sources that could have long term, cumulative impacts, leading to chronic human health problems; as, in the long term, these could cost more to the health services than acute cases resulting in death (Rogan, 1992; Rice, 1997).

There are statistically significant, higher incidences of cancer amongst groups exposed to dietary sources of organic pollutants (Bernes, 1998). Fishermen in Sweden eating contaminated fish have been shown to have higher levels of stomach cancer and squamous cell carcinoma than those eating uncontaminated food (Svensson *et al.*, 1995). One problem is that it can take up to 20 years for the cancer

to develop and exposure to other pollutants can mask results in some cases and amplify them in others (Borgert, 2004).

It has long been known that PAHs and PCBs can cause cancer, e.g. respiratory exposure can lead to lung cancer and it is likely that other cancer types can be linked to dietary exposure *via* contaminated food sources. Reproductive problems are also associated with organic pollutants. For example, after the Japanese rice oil incident levels of miscarriage increased and the number of boys born in the following years were abnormally low. Those that were born had a higher than average chance of having abnormally developed sexual organs and, later on in life, a low sperm count (Bernes, 1998).

Eight PAHs have been classified as highly carcinogenic and mutagenic (chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene (Menzie *et al.*, 2004). BaP has been shown to be one of the most toxic of the PAHs (Kuo *et al.*, 1998). Not all PAHs have the same mode of action, therefore different ones may have different health effects. Much of the data on the human health impacts of PAHs have been inferred from data generated from mixtures of PAHs rather than exposure to individual PAHs. However, in assessing potential disease incidence caused by environmental exposure to PAHs, this is not really a problem as most human exposure will be to a mix of these chemicals anyway.

Gupta *et al.* (1993) showed workers in a rubber factory exposed to BaP had statistically significantly reduced lung function in relation to their length of employment and showed symptoms such as breathing problems, chest pains, bloody vomit and throat irritation. Higher levels of lung cancer have been observed in women in China using smokey coal in unventilated homes, as compared to those using natural gas and wood (Mumford *et al.*, 1993). A number of studies have shown lung cancer effects linked with exposure to mixtures of PAHs: including roofing-tar emissions (Hammond *et al.*, 1976) and coking ovens (Lloyd, 1971; Mazumdar *et al.*, 1975; Redmond *et al.*, 1976). Several authors have reported increases in skin tumours amongst mice exposed to PAHs including benzo[a]anthracene (Bingham and Falk, 1969). benzo[b]fluoranthene (Habs *et al.*, 1980), benzo[a]pyrene

(Warshawsky *et al.*, 1993), chrysene (Warshawsky *et al.*, 1993) and dibenz[a,h]anthracene (Platt *et al.*, 1990).

A number of studies have shown have shown that PAHs can also act as initiators of cancers by pre-conditioning cells to react to other stimuli, Cavalieri *et al.* (1988), with benzo[a]pyrene, Levin *et al.* (1984) with benzo[a]anthracene, Amin *et al.* (1985) with benzo[b]fluoranthene, LaVoie *et al.* (1982) with benzo[k]fluoranthene, Slaga *et al.* (1980) with chrysene and dibenz[a,h]anthracene and Rice *et al.* (1985) with indeno[1,2,3-c,d]pyrene.

There are considerable concerns about the effects of persistent pollutants on the central nervous system and intellectual development. Unfortunately, effects can be weak and very difficult to measure in individuals and are often only apparent in population studies. Effects on the developing foetus can be the most serious, as this is the most sensitive stage of development and exposure to a particular pollutant at a particular stage of development can be catastrophic to either physical or mental development or both (Damstra, 2002; Perera, 2002; Ostrea, 2002; Lee, 2003). Again, many of the data for this have been gathered from acute exposure incidents (Japanese rice oil disaster) where it has been shown that children born to exposed mothers had a lower birth weight and slower growth than non-exposed children and are prone to more behavioural problems such as apathy. They also seem to exhibit a lower than average intelligence and poor memory skills. Similar problems have been seen in groups where the parents have been exposed to lower doses than in Japan. Children of anglers who regularly ate fish from Lake Michigan exhibited lower birth weight and reduced reflex development along with lower IQ and impaired reading skills which were still apparent at the age of 4 (Jacobson, 1996a; Jacobson, 1996b; Bernes, 1998; Darvil, 2000; Rylander *et al.*, 2000).

PCBs and PAHs can take a long time to accumulate in the body, so it is vital to consider chronic exposure levels when trying to establish the risk to any group, particularly foetuses and newborn children who can get a very high dose *via* the placenta and breast milk respectively (Koppe *et al.*, 2000; Koppe and De Boer, 2001; ten Tusscher *et al.*, 2003). Studies in the Netherlands have shown a relationship between 'normal' exposure to PCBs and dioxins *via* breast milk contamination and a

reduction in birth weights, immune responses, thyroxine levels and neurological maturity in newborn babies – in this study no long-term reduction in learning ability was found. It should be noted that not all effects will occur in every case and that in many incidents it may be a combination of pollutants that are responsible, e.g. high levels of PCBs are often associated with high levels of other contaminants, such as dioxins (Eskenazi *et al.*, 2000; Koppe *et al.*, 2000; Koppe and De Boer, 2001; Rylander *et al.*, 2002; ten Tusscher *et al.*, 2003).

1.6.2 Metals

Many metals are known to be toxic, causing oxidative stress and inflammation (e.g. Ni), and it is thought, that when present in an ultrafine state, the greater surface area might lead to a greater toxicity (Maynard, 1999). This would mean that sediment contaminated with heavy metals could have the potential to aggravate or induce health problems amongst those regularly exposed, if these pollutants can be shown to be remobilised into the atmosphere, hydrosphere or food chain.

Aluminium is the third most ubiquitous element on the planet and is found in air, soil and water. Inhalation exposure tends to occur in the workplace (non-workplace inhalation exposure in minimal) and even those exposed to high levels (e.g. 10mg/m^3), e.g. welders, exhibit no obvious signs of toxicity (De Voto and Yorkel, 1994). Ingestion is the most common route of exposure, as Al adheres to many processed foods and is present in many medications, e.g. Al containing antacids. Ganrot (1986) estimated that man ingests approximately 30-50 mg a day, of which around 1% is absorbed (taking Al buffered medication can enhance this several times, as can the form of Al ingested). The presence of citrate also increases absorption. Aluminium has been shown to affect learning, memory and motor control in cats and rabbits, with severe conditions resulting in eventual death of the subject. It also adversely affects neural pathways leading to degenerative neurological conditions such as Dialysis Dementia (caused by the high levels present in the fluid used for kidney dialysis) (Plats, 1981; Klaassen, 1999).

Arsenic is used in the production of glass and ceramics, for bronzing, in the production of insecticides, herbicides and in wood preservation. Inhalation can lead to respiratory tract illnesses such as bronchitis and laryngitis (Ishinishi *et al.*, 1977;

Landrigan, 1981; Nemery, 1990) and in high concentrations can damage the digestive tract, heart and circulation. Studies suggest that arsenic is associated with skin cancer (Klaassen, 1999) and other internal cancers such as liver, lung, bladder and kidney (Bates *et al.,* 1992; Chen *et al.,* 1992, Chiou *et al.,* 1995). Chronic exposure can lead to a reduction in nerve conductivity velocity (Lagerkvist and Zetterland, 1994) and hepatic injury (Lander *et al.,* 1975) along with vascular problems and changes in skin pigmentation.

In humans cadmium is carcinogenic, mutagenic and teratogenic (Friberg *et al.,* 1986b; Fischer, 1987; Kazantzis, 1987; Heinrich, 1988). It has a relatively long biological half-life (10-15 years), so chronic low-level exposure can cause long-term health problems (Jarup *et al.*, 2000). It can cause kidney damage (Friberg *et al.,* 1986a), pulmonary disease, renal inflammation and fibrosis, and hypertension, as well as various skeletal conditions such as osteoporosis (Klaassen, 1999).

Chromium, although an essential element, can be toxic at higher levels; as found in industrial exposure, causing hepatic peroxidative damage. Very large amounts can cause ulcers, liver, and kidney damage. Some chromium compounds cause tumours in the respiratory and nasal tract (Klein, 1996; Klaassen, 1999). It is widely used in a variety of industrial processes (e.g. aluminium cookware manufacture, leather tanning and as a wood treatment agent).

Copper has the potential to cause metabolic disorders, indian childhood cirrhosis and chronic cholestatic conditions. Symptoms of copper poisoning are headaches, hypoglycemia, increased heart rate, nausea, copper deposits in the brain and liver causing damage to the kidneys. In children it is associated with hyperactive behaviour, learning disorders such as dyslexia, attention deficit disorder and infections. Symptoms of copper toxicity include autism-type symptoms, depression, hallucinations, hyperactivity, insomnia, disperception of the senses, time, body, self and others, paranoia, personality changes, psychosis and schizophrenic type symptoms (Klaassen, 1999).

Iron in very high doses can lead to liver function problems, diabetes mellitus, endocrine disruption and cardiovascular effects (Klaassen, 1999).

Lead can cause neurological disorders in humans, particularly in children and the foetus, where it is thought that there are no safe levels of exposure. These can lead to behavioural disorders and intelligence impairment (Lansdown, 1986; Needleman, 1987; Needleman *et al.,* 1996), as well as decreased auditory sensitivity in children and decreased visuomotor performance in preschool children. It can also cause haematologic conditions such as anaemia, renal conditions, elevated blood pressure and reproductive disorders and is carcinogenic (Finkelstein *et al.,* 1998; Klaassen, 1999).

Manganese maybe neurotoxic at high levels, affecting the brain's dopamine system but the mechanisms are not well understood (Tran *et al.*, 2003). It can also cause respiratory conditions, damage to the central nervous system and behavioural problems (Klaassen, 1999).

The toxic properties of mercury have been known of since the time of the Roman Empire. It is an important industrial chemical used in a variety of processes, including the manufacture of chlorine gas, as a fungicide and in dental filings. Exposure can lead to CNS damage, lung damage and renal disease (Vroom and Greer, 1972; Jaffe *et al.*, 1983; Rowens *et al.,* 1991; Bluhm *et al.*, 1992[a,b]; Boogaard, 1996). The form that is most problematic in the environment is methylmercury. It can be created in the environment from elemental Hg by bacteria and is highly toxic and biomagnified in the food chain, although exposure to UV can detoxify it (Ullrich *et al.*, 2001).

Nickel exposure is one of the most common reasons for skin complaints (contact dermatitis) in humans (WHO, 1991). Nickel is carcinogenic and very high levels can affect heart, kidneys and lungs (Klaassen, 1999).Zinc poisoning can lead to gastro-intestinal problems and lung disease (Samman and Roberts, 1987; Klaassen, 1999).

1.6.3 Mixtures of Chemicals

As can be seen from the above text, many of the metals and organic compounds we are exposed to on a regular basis cause the same disease effects. This can mean that, when investigating population environmental exposure, it is incredibly difficult to

confirm whether or not an individual chemical is responsible for disease incidence or whether (as is more likely with low dose chronic exposure) it is a mix of chemicals. In recent years the relevance of 'cocktails' of chemical has become a focus for many investigating environmental chemical exposure and its effects on human health (Simmons, 1995; Kortenkamp, 1999; Walter *et al.*, 2002; Borgert, 2004; De Rosa *et al.*, 2004; Kortenkamp, 2007). Chemicals can act together in a variety of ways, many have similar modes of action, targeting the same molecular pathways in the body (e.g. polychlorinated dioxins and furans) (van den Berg *et al.*, 1998). Other substances have dissimilar modes of action targeting different molecular pathways within the body (Kortenkamp *et al.*, 2007). There are five main ways that a mixture of chemicals can behave within the body.

1. Synergism: A mix of chemicals will produce a larger effect together than each would do separately and, therefore, lower concentrations of each chemical are required to have a toxic effect (Borgert, 2004).
2. Antagonism: A mix of substances will have less of an effect than each of the individual chemicals on their own (Borgert, 2004). If this is the case, then higher concentrations of each chemical are required to have any effect. It is possible that in a complex mixture the actions of those behaving synergistically and antagonistically will cancel each other out.
3. Potentiation: This occurs when exposure to one chemical enhances the effect of another chemical. The effect will be similar to that of synergistic chemicals, but the mode of action (molecular pathways) may be different.
4. Additivity: The combined effects of a number of chemicals are the sum of those of the individual chemicals (Kortenkamp, 2007)
5. No effect

Most of the toxicological testing that takes place is done either on single chemicals or specific mixtures that are related to specific discharges, e.g. a factory discharging a known combination of chemicals. Due to the complexity of mixtures that are present in the environment it is impossible to test all of the potential interactions that occur on a regular basis and predict how these will influence human health (Borgert, 2004).

1.6.4 Particulate Matter and Disease

In recent years it has been discovered that reduction of particle size can lead to materials which had been thought to be chemically inert becoming highly reactive and therefore, potentially damaging to human health (Maynard, 1999). Research conducted by Dockery *et al.* (1993) and Seaton *et al.* (1995) suggests a link between exposure to PM_{10} particles and cardiovascular disease, as do Jefferson and Tilley with their work on transition metals (Maynard, 1999). Studies into titanium dioxide and carbon black have shown that both become more toxic when present as ultrafine (<100nm) particles. Recent studies have shown that 60% of 20nm particles inhaled are deposited and remain in the gas exchange zone of the lungs (Maynard, 1999).

A large percentage of the smaller particulates found in the atmosphere come from industrial processes, incineration of waste and vehicular emissions, and many of these processes involve the production and emission of heavy metals and organic pollutants (e.g. PCBs) (Buonnano *et al.*, 2009). It is well known that metal and organic pollutant concentrations in sediments increases with decreasing particle size (Murray, 1999) which could mean that the health problems associated with heavy metals are likely to be amplified by those associated with decreasing particle size.

1.7 Chapter Summary

Previous studies on the Mersey Estuary and surrounding area have shown that there are elevated concentrations of a number of pollutants in the sediment and water. Many of these substances have the potential to cause significant health impacts to populations exposed to them It is important therefore to investigate the concentrations of potentially toxic substances in the environment in order to assess whether or not there are risks to the local populations.

CHAPTER 2
METALS AND ORGANIC POLLUTANTS IN ESTUARIES AND LAKES

The following chapter examines the behaviour of metals and organic pollutants in estuaries and lakes. It first considers how wetland processes, physical (e.g. wave action, bioturbation etc), chemical (e.g. diagenetic remobilisation) and temperature and salinity, influence the behaviour of the sediments and their contents. The second section investigates the differences in behaviour of metals in estuaries and lakes, and the final section discusses Persistent Organic Pollutants in the environment.

2.1 Wetland Processes and Their Influence on Pollutants

Saltmarshes and wetlands, as well as being very important habits, are also important sources of nutrients and natural coastal defences (Allen, 2000). They are relatively flat areas of land, subject to periodic flooding and are often poorly drained. Development is a result of sediment deposition gradually increasing their elevation and the time that they are exposed to the atmosphere. This allows vegetation to develop, usually halophytic plants of varying kinds, e.g. *Spartina* spp. These, in turn, trap more sediment and increase the rate of development of the saltmarsh. Saltmarshes usually have an area of mud flats between them and the main water body, which supplies sediment and acts as a means of wave dissipation. The higher up on the marsh the location is, the less it is subjected to tidal inundation. Saltmarshes with good vegetation cover are more stable and less prone to post-depositional changes affecting pollutants within the sediments and, therefore, provide an excellent record of historical pollution in the area (Plater *et al.*, 1998, Fox *et al.*, 2001). Many of these pollutants preferentially adsorb to the fine sediments which are particularly prevalent in saltmarsh sediments (Olsen *et al.*, 1982).

Many studies have shown that sediments preserve records of historical pollutant input to an area (Beuskens *et al.*, 1993; Huntley *et al.*, 1995; Fox *et al.*, 2001), which can come from a variety of sources, both natural and anthropogenic. Saltmarsh, mud flat and lake sediments are sinks for heavy metals and other pollutants such as PCBs (Polychlorinated biphenyls) and PAHs (Polycyclic Aromatic Hydrocarbons)

(Forstner and Salomons, 1980; Orson *et al.*, 1992; Valette-Silver, 1993). This is particularly important as many wetlands are near to areas of heavy industrialisation and hence are likely to receive discharges of pollutants associated with these industries (Cacador *et al.*, 1996).

2.1.1 Physical Processes

Physical disturbances, e.g. bioturbation and wave action, can reoxidise anoxic sediment (O'Reilly Wiese *et al*, 1995). Plants can influence the depth to which oxygen penetrates as their leaves transport oxygen from the atmosphere to the roots. This can induce a localised oxygen environment around the root systems and can lead to localised heavy metal enrichment around roots (Vale *et al.*, 1990) and affect the availability of metals ions (Williams *et al.*, 1994).

As well as direct anthropogenic inputs to the aquatic system, pollution levels can be affected by a variety of other factors. Dredging a channel can remove huge amounts of sediment and, therefore, any associated pollutants (Gil *et al.*, 2010). Some of these will be released back into the environment and some will remain associated with the sediment. Those that remain in the sediment will be redeposited (with the potential to be remobilised) at the location where the dredged material is dumped. Any construction work that disturbs the sediment, for example, a harbour development, can release pollutants back in to the water column. These will then often settle out elsewhere in the estuary causing a spike in recorded levels. Natural processes such as sea-level rise and storm events can also lead to sediment erosion and redistribution (Williams *et al.*, 1994).

There is a constant input of natural trace metals from the geochemical weathering of rock which can account for the low background metal content in sediments. Various elements come from seawater (Na, K, Mg, Ca as well as chloride, sulphate, bicarbonate and carbonate ions) (Williams *et al.*, 1994). Major nutrients (nitrogen, phosphorus and carbon) come *via* riverine input (Bourg, 1988), as do Si, Al and transition metals. Inputs can vary with season, with mineralogical inputs dominating in winter and organic inputs dominating in summer due to higher productivity. However, a percentage of trace metals in estuarine sediment come from

anthropogenic sources, e.g. mining or dumping of industrial waste. This input can be direct (dumping) or indirect, e.g. from river runoff or atmospheric sources (Rae *et al.*, 1997).

Many pollutants (both organic – e.g. PCBs, and inorganic – e.g. heavy metals) are preferentially found in fine sediment deposits and their presence in the sedimentary record is therefore controlled by sedimentary processes (Olsen *et al.*, 1982). Particle size distribution is related to sediment input to the estuary and a combination of tidal and wave-induced flows. If there are higher pollutant levels associated with finer sediments (Taylor, 1986), then processes that lead to higher or lower than normal input or removal of fine sediments will affect levels within the sediment. For example, during exceptionally wet weather larger volumes of water will pass through the system and less deposition may occur during that time. This is due to the fact that as the flow velocity decreases, progressively finer sediments settle from suspension. Hence, when the fine grain sizes are kept in suspension by higher flows, the recorded pollution levels will appear to decrease. This will lead to a drop in recorded pollution levels within the sediment for that period. The opposite is also true; in periods of very low flow there may be a spike in pollution within the sediment as more fine particles can settle out. Tidal deposits often show variations in grain size linked to tidal height and velocity (i.e. spring and neap tides) (Stupples and Plater, 2007). Sediment particles in the upper marsh sediments are usually fine grained and rich in organic matter due to the effect of estuary infilling and the development of vegetation cover which often means they exhibit high levels of pollutants (Williams *et al.*, 1994).

2.1.2 Chemical Processes

Metals can enter an area in both dissolved and particulate forms and may eventually settle out to become incorporated into the sediment (Cacador *et al*, 1996). Sediment deposited pollutants can be reintroduced to the environment by resuspension and mixing of the sediment. Remobilisation of pollutants from other areas within an estuary can lead to erroneous contaminant levels being recorded in a different area, as they settle out. This may suggest higher levels of pollutant input than actually occur (Valette-Silver, 1993). Once deposited, diagenetic processes control the behaviour of the metals, e.g. pH, redox conditions, organic matter content and

sediment composition, (Zwolsmann *et al.*, 1993). Diagenesis can remobilise pollutants, e.g. trace metals, particularly Mn and Fe. In the anoxic parts of the sediment they can become soluble, which allows them to move and be redeposited in the upper oxic parts. This can lead to a seeming increase in contaminants in the surface layer which could be misinterpreted as an increase in pollution input when, in fact, it is due to redistribution of contaminants already in the sediment (Valette-Silver, 1993).

Metal concentrations are influenced by anthropogenic inputs, parent material, organic matter particle size and diagenesis. Manganese depletion in the top few cm of the sediment is common and thought to be due to liberation of Mn^{2+} oxides due to reduction of Mn oxides (Nixon, 1980). Metals such as Se, As, Hg, Pb, and Sn can be lost from the sediment due to volatilisation cause by alkylation (Weber *et al.*, 1991; Williams *et al.*, 1994). During degradation by bacteria metal sulphides are converted to sulphates which are more reactive. However this process also releases sulphuric acid which lowers the pH of the sediment and may prevent the precipitation and the availability of the metals (Giblin and Howarth, 1984). Metals released by sulphate reduction are generally as metal sulphides which are of low solubility and as long as they remain that way, are limited in their availability for biological or chemical uptake (Williams *et al.*, 1994).

Decomposition of organic matter is greater near the surface of the sediment as there is higher exchange of oxygen with the atmosphere. Deeper in the sediment anoxic conditions occur which allow anaerobic bacterial degradation to occur (Williams *et al.*, 1994). The presence of organic matter can increase the uptake of metals to the sediment by metal-organic complex formation. These can be very strong and actually limit the bioavailability of the metals within the sediments as long as the physico-chemical conditions remain constant (Orson, 1992).

2.1.3 Temperature and Salinity Effects

Temperature (and hence season) affects the microbial activity within the sediment, with lower temperatures leading to less bacterial activity. This limits sulphate reduction and allows oxygen penetration. Higher temperatures increase microbial activity which allows the reduction of Fe/Mn oxyhydroxides and the release of

sorbded metals (Hines *et al.*, 1984). Submergence of the marsh by the tide will affect metal mobility as an increase in salinity can increase the solubility of metals such as Cd and Zn (Palheiros *et al.*, 1989) and will also affect oxygen levels. Salinity also influences adsorption and desorption reactions with organic matter, flocculation of colloidal particles and precipitation reactions within the sediment (Kerner and Willmann, 1992). For example, lower salinities favour the release of sediment Cr to the water column (Abu-Saba and Flegal, 1995; Comber *et al.*, 1995). Temperature can also affect the water levels in shallow lakes which may dry-up in warm weather. This can lead to oxidation and geochemical remobilisation.

Coarse material is deposited in high-energy conditions and is generally less contaminated than finer material, hence the most polluted sediments are usually found in low energy areas (Forstner and Salomons, 1980).

Fine-grained sediments have high adsorption capability and therefore store a record of contamination inputs to a wetland area (Cauwet, 1987, Araujo *et al.*, 1988). These have been used as a source of information regarding historical contamination inputs, both in freshwater and marine environments, since the late 1970s, alongside the discipline of ^{210}Pb dating. Fox *et al.* (1999) state that for a sample location to be representative of the pollution inputs to an area, the sedimentation rate must have been fairly consistent for a relatively long period of time.

2.2 Metals in Wetland Environments

There are three main sources of heavy metals to the environment and sediment; natural processes (geological weathering and biological decomposition), material brought in *via* the tide, land runoff, atmospheric fallout and biological productivity and, anthropogenic inputs from human activities such as mining, industrial ore processing, sewage, waste runoff and incineration (Valette-Silver, 1993; Deely and Ferguson, 1994). Metals can be present in the water column both in solution and associated with particulate matter such as suspended sediment. Within the sediment metals are present in a number of forms – mineral lattices (residual phase), associated with particle surfaces (controlled by grain size and surface area), oxides, sulphides, metal carbonates and organometallic compounds (Lopez-Sanchez, 1996;

Rae, 1997). The form they occur in will affect their bioavailability and potential for remobilisation.

2.2.1 Metals in Estuaries

Spatial fluctuations in an estuary will depend on the number of point source emitters and the degree of mixing within the estuary (there should be less variation in a well mixed estuary). Temporal variations in both the pollution load and the sedimentary environment can be caused by increased water flow and seasonal production of organic matter which can be related to phytoplankton blooms and bacterial activity. Wright and Mason (1999) and Rae (1997) found that levels of metals vary with season. They are highest in material deposited in winter and lowest in that deposited in summer. Sediment profiles often reflect global pollutant inputs and are related to the nature of the sediment (grain size, organic carbon content, and mineralogy) and the diagenetic influences. Tidal and wave action sort the sediment and also influence the diagenetic processes (Rae, 1997).

A study by Buckley *et al.* (1995) of Halifax harbour (Nova Scotia) identified a variety of sources for pollution. These included sewage outfall and industrial waste (dominated by metals and organic carbon), leaching from landfill sites and shipbuilding activities (Zn, Pb, Ni, Cu and reducible forms of Cu), diagenesis (which accounted for Si and three forms of Mn) and surface drainage and river input processes (which brought in Li, Al, Mg, Fe and some forms of Mn bound with fine grained, organic rich sediments). The predominant factor controlling metal input in each case was related to the location of the sampling sites. The study showed that at each location there were often changes in the dominant process over time, usually associated with the influence of the environment and humans, for example, new sewage inputs, or regulation of discharges. The study was aided by high sedimentation rates and reducing conditions in the sediment which limited bioturbation at the sites chosen and hence limited disturbance of the sedimentary record. However, physical disturbance due to shipping propellers was a problem in some locations, as this disturbed the sediments and therefore the chronology of pollution.

A study of the Mersey estuary by Martino *et al.* (2002) found a positive relationship between dissolved Co and Ni which indicating a common source. The presence of Cd, Co, Cu, Ni and Pb associated with suspended particulate matter indicated resuspension of metals from the sediment. This could have been due to pH changes, fluctuation of redox conditions and bacterial or chemical degradation of particulate organic matter. They suggested that the contaminated sediment was an important source of metals to the water column and would be for some time to come (decades) due to the desorption processes slowly liberating metals from the sediment.

It is often very difficult to distinguish between natural background metal levels and pollution levels, due to the variability of the natural background levels. Natural variations can be due to particle size, mineral composition and post-depositional processes at any location (Beeftink *et al.*, 1982). It is possible to use Average Shale Values (Turekian and Wedepohl, 1961) as a method of estimating natural background metal levels as these give a midrange ideal value. However, Average Shale Values do not take into consideration local factors such as grain size effects and may over-estimate certain metal levels (As, Cd, Cr, Cu, Hg, Ni, Zn). Consistently low downcore metal levels could indicate that the metals present are at background levels rather than due to pollution inputs. An obvious decline of metal levels with depth could indicate that the sampling has reached pre-industrial levels (O'Reilly Weise *et al.*, 1995, 1997).

Generally as sediment grain size decreases the metal concentration increases, as metals bind more easily to silt and clay particles (Thorne and Nickless, 1981; Cauwet, 1987; Araujo *et al.*, 1988). O'Reilly Weise *et al.* (1995) found that metal concentration increased as particle size decreased in sediments from two Essex estuaries. Work done by Taylor (1986) suggested a link between organic carbon and silt content and trace metal concentration within the sediment and seemed to show that distribution of metal contaminants within the Mersey estuary were related more to silt concentration than to the input sites.

Aluminium content generally will increase along with the percentage of silt and clay in the sediment. However, the presence of fecal pellets in sandy sediment will also keep its levels high (as fecal pellets often consist of aggregated sand and clay).

Higher levels of Al compared with K often indicate the clay mineralogy in the sediment, therefore fluctuations in Al with depth can show a fluctuation in the amount of clay in the sediment (Velde *et al.*, 2003). A relationship between Al and Zn indicates that Zn may be related to clay content. The levels of Co, Cr, Cu, Ni, V and Zn can be controlled by the proportion of combined silt and clay in the sediment (Evans *et al.*, 2003).

Metals in estuaries are generally present 3-5 orders of magnitude higher in the particulate form than in the dissolved form and therefore accumulate in the sediment (Balls, 1989; Coomber *et al.*, 1995). These metals may eventually be re-released to the water column either by diagenesis (Petersen *et al.*, 1995) or as a result of physical disturbance (Boughriet *et al.*, 1992).

Variations in sediment metal concentrations with depth could be due to variations in inputs (e.g. reduced pollution) or to the post-depositional migration of metals. High Mn in the surface layers could be due to formation of Mn oxyhydroxides in oxic conditions instead of anthropogenic pollution (O'Reilly Weise *et al.*, 1995). A strong peak in Mn or Fe may indicate their mobilization in redox conditions (and any trace metals associated with them) (Cundy and Croudace, 1995). Low values of Mn in sediment samples could indicate low levels of oxygen in the sediment, as in anoxic conditions Mn is more likely to partition to the soluble phase (Gobeil *et al.*, 1981). An increase could indicate an improvement in estuarine water quality and *vice versa.* This is also true of Fe but to a lesser extent as Fe requires lower oxygen levels than Mn to dissolute (O'Reilly Weise *et al.*, 1997). An increase in Mn and Fe with depth could be due to their being trapped by authigenic carbon / sulphide formation (Cundy and Croudace, 1995). Higher Mn than Fe could indicate concentration in the estuarine environment; low Mn to Fe could indicate diagenetic loss through reduction (Velde *et al.*, 2003).

Calmano and Forstner (1983) have stated that $Fe^{(III)}$ and $Mn^{(IV)}$ hydrous oxides are the major hosts of trace metals in estuarine sediments. They are important sources for bioavailable metals as, when they are reduced during early diagenesis, they form soluble $Mn^{(II)}$ and $Fe^{(II)}$. When sulphate reduction occurs they may be reduced to monosulphides and pyrite. If oxidising conditions occur, for example, by disturbance

of the sediment, then there is the potential for metals to be remobilised. Cr, Pb and Zn do not partition strongly into pyrite so have the potential to be remobilised back to the water column. Mn oxides are particularly important for Cd binding (Martino *et al.*, 2002). Fe oxides decrease with increasing grain size (Lick, 1986).

Speciation of metals is a very important method of assessing the potential toxicity of those present, as their physicochemical form will determine their bioavailability and potential for remobilisation. Lam *et al.* (1997) found that for Cr the reducible metal phase (bound to Fe and Mn oxides) was the most important followed by the binding to organics and sulphide fraction. For Cu the organics and sulphide was the most important fraction in the more polluted harbour. In a less polluted estuary there was a higher proportion of Cu in the exchangeable and reducing fraction. The speciation of Ni was less clear-cut. However, there was a difference between sediments from cleaner areas and more polluted areas overall. Other factors that affect speciation are salinity, pH, dissolved oxygen, amount of dissolved organic matter, sediment composition and microbial activity. In the above study total sulphide content seemed to have a significant effect on the metal speciation. As it increased the reducible metals phase became the most important for Cr and Ni and as it decreased the exchangeable and carbonate phases became the most important for all 3 metals.

An increase in S can indicate bacterial reduction of sulphate. Sulphur often shows a peak just above the sulphate reducing zone (Rae, 1997). There may also be a trace element peak associated with the sulphur, due to precipitation of insoluble metal sulphides (McCaffrey and Thomson, 1980; Zwolsman *et al.*, 1993). If these peaks are inconsistent then a stable redox zone is unlikely to have established. This could be due to frequent flooding of the site. If a correlation is found between Fe and S it can indicate the formation of Fe-sulphides. A concentration minima of Pb might coincide with sulphide increase and be due to mobilisation of Pb due to hydrous Fe and Mn oxide breakdown. Peaks that do not associate with other redox-sensitive elements often indicate anthropogenic input (Cundy and Croudace, 1995).

Sediment particles in the water column increase the rate of soluble iron precipitation which forms iron hydrous oxides on the particles. These are efficient scavengers of other trace elements, removing them from the sea water and allowing their deposition

into the sediment. The amount removed will be greater in areas of small particles which have a relatively larger surface area (Aston and Chester, 1973). An increase in salinity also increases the rate iron is also removed from sea water (Boyle *et al.*, 1977).

Ni preferentially partitions to the dissolved phase irrespective of redox conditions. So values should remain relatively constant in sediments (obviously depending on relatively constant inputs), it can, however, rapidly desorb in low salinities (O'Reilly Weise *et al.*, 1997).

Organic matter and humic acid, in particular, are known to take up appreciable quantities of trace metals. Binding to organic matter can be due to physical adsorption (which is a weak force allowing the metal to be replaced relatively easily) or to strong adsorption by the formation of chemical interactions between the metal and the organic matter, forming insoluble compounds with a low mobility. It is possible that metals lost from organic matter may be lost from the sediment record which would affect the accuracy of the sediment in reflecting historical pollution inputs (Rae and Allen, 1993). Cacador *et al.* (1996) found material trapped between plant roots on the saltmarsh contained less mobile forms of Zn, Pb and Cu. Eventually, it is thought that these metals may adsorb to clay particles and become less mobile. However should they desorb with depth they will become more mobile (Cacador *et al.*, 1996).

Total organic matter concentrations should decrease with depth as bacterial action degrades the organic matter. High levels of organic carbon/matter could be due to terrigenous input (Jones and Turki, 1997) or due to the fact that as estuaries infill they emerge above the high tide levels and more vegetation can become established. Cu often forms stable compounds with organic matter (Hudson-Edwards *et al.*, 1996). A large correlation of any metal with organic matter and sulphide compounds could indicate that it is present in the oxidising fraction (Morillo *et al.*, 2004). Trace metals are also remobilised due to changes in redox potential, e.g. Mn. Redox potential is one of the most important factors in the way metals behave in sediments, and is dependent on the depth to which the sediments are oxic. This can be affected by the amount of waterlogging in the sediment or saltmarsh, so areas that are more

likely to be submerged will have less chance of being oxic. Sediment with larger grain sizes will allow the water to drain away more quickly and therefore allow more oxygen penetration (Jones and Turki, 1997).

Unlike lakes (see Section 2.2.2, 'Metals in Lakes'), acidification does not occur in the estuarine or coastal environment, however, other potential problems exist in the form of biological mixing by burrowing organisms and physical mixing due to wave action. In areas of high sedimentation rates, coarse particle deposition and the influx of particles from the marine environment can dilute or even remove evidence of pollution inputs. This is less likely to occur in areas of high influx of fine-grained sediments (Valette-Silver, 1993).

2.2.2 Metals in Lakes

As with estuaries, metals enter lakes in a variety of ways. The majority of metals entering the lacustrine environment naturally do so *via* surface runoff scavenging material from the catchment and through groundwater input. A proportion are also deposited from atmospheric fallout. It has been estimated that lake sediments retain between 40% and 60% of the pollutant metals that enter them (Nriagu and Wong, 1986). These processes are responsible for the pollution of lakes with metals, along with direct input from human processes such as dumping, point source emissions from industrial processes such as ore smelting and burning fossils fuels. For example in Sudbury, Ontario a number of studies have been carried out showing the relationship between Cu (and other metals such as Ni and S) contamination in the sediment and the rise and decline of the local smelting industry (Nriagu and Rao, 1987: Gunn, 1995).

A certain amount of metals (e.g. iron) are required by lake organisms. However, there is a concentration above which the metals cease to be useful and become toxic to these organisms. As metals are often adsorbed onto sediments (in similar ways as in the estuarine environment) the concentrations are usually higher than those in the overlying water column (Rognerud and Fjeld, 2001). Once deposited they are subjected to post-depositional processes such as diagenesis and biological mixing leading to redistribution and potential concentration within the sediment (Boudreau, 1999). Rognerud and Fjeld (2001) found that several metals (Sb, Pb, Bi, As, Hg and

Cd) were significantly enriched in the surface sediments (up to 7 times those found in the bottom sediment) of Norwegian lakes. Cu, Zn and Ni concentrations also increased, though not to the same extent. In this case, due to the sampling method employed, it was decided that the enrichment was caused by atmospheric deposition, diagenetic processes and accelerated release of these elements from the catchment. Blais and Kalff (1993), in a survey of 47 lakes in Canada, showed that the enrichment of Pb in surface sediments was as much as 14 times that of natural background levels, and that only approximately 7% of this Pb could be accounted for by natural sources.

Lake sediments are very sensitive to acidification (due to their low buffering capacity) which can affect the behaviour of the pollutants within the sediment. Transition metals, in particular, can be remobilised under low pH conditions which leads to their being redistributed though the sediment or liberated back to the water column (Valette-Silver, 1993). Aluminium is particularly affected by changes in pH and, therefore, Al distribution in sediment can be affected by lake acidification giving potential problems with the interpretation of Al levels. This can also be true of Zn (Carignan and Tessier, 1985). Naturally alkaline lakes such as those in Noril'sk, Siberia can actually limit the environmental impact of metal pollution as they reduce the bioavailability of the metals (Michelutti *et al.*, 2001). In the summer months lakes may also stratify, with oxygen-rich waters at the top and reduced waters at the bottom. This will lead to the bottom sediments having a different geochemistry to when the lake is mixed after the autumn turn-over.

As with estuarine sediment Mn and Fe profiles are affected by post-depositional diagenetic processes, leading to a redistribution of these metals within the sediment (Belzile and Tessier, 1990; Davison, 1993). Due to its strong affinity with Fe, As profiles often exhibit a similar distribution to those of Fe (Belzile and Lebel, 1986; Belzile and Tessier, 1990) Other factors affecting metal distribution within the sediment are the characteristics of the lake itself, both physical and chemical. For example, the drainage profile of the surrounding land and the number of streams coming into the lake will influence how much pollution is brought into the lake and how much is washed out, as will the sedimentation rate and the degree of bioturbation within the lake (Belzile *et al.*, 2004).

There are a number of natural sources of mercury to the environment including volcanic eruptions, local weathering and release from the oceans. Ramamoorthay (1985) estimated that human activity in the 20th century has released Hg at an order of magnitude higher than natural sources would have. Hg is released to the environment *via* a number of processes including the burning of coal, the alkali industry, waste incineration and mining. Lockhart (2000) showed that Hg mobility in sediment *via* diagenesis is limited.

A study of heavy metal pollution resulting from mining and smelting activities in three reservoirs along the Lot river in France (Audry *et al.*, 2004) showed that the sediment was contaminated with Cd, Zn, Cu and Pb at levels well above that of the natural background levels for the area. Cadmium was enriched by a factor of 300 and Zn by a factor of 65 in selected locations. The historical profiles established could be matched to the pollution history of the area. They showed the onset of mining and smelting, recorded the evolution of the industry in the area and the different methods of treatment of the waste and also showed one-off 'accidental' pollution incidents.

The source of anthropogenic pollution in lakes can be either local (waterborne or atmospheric deposition related) or global input *via* atmospheric transport. However, metals can also be present due to natural processes (weathering of rocks). Tylmann *et al.* (2001) found a correlation between Pb, Zn and LOI in Polish lakes. Many studies have shown a correlation between fine grained lake sediment and pollutant metals (Forstner, 1977).

A study by Nienke and Lee (1982) indicated that Zn is adsorbed by lake sediment and becomes tightly bound to it, therefore high levels of Zn in lake sediments are not necessarily a hazard to aquatic life, as it is difficult to remobilise once bound to the sediment. They also showed a link between Zn and organic matter and that Zn was released from the sediment as the pH lowered.

Sly (1984) showed that in lake and river sediments there was an association between P and fine grained sediments and Pb and organic carbon. He found an association between coarse grained sediment and Fe and Zn which was suggested to be because

these metals are present as coatings on the sediment. Ni and Cu appeared to be related to Fe concentrations. Hg was strongly associated with S and organic carbon and bound to Fe oxyhydroxides.

Arsenic has been shown to accumulate in the surface layer of lake sediment due to its association with Fe and Mn oxyhydroxides (Takamatsu *et al.*, 1985). Similarly, Cd, Cu Pb, Zn, and Ni have been shown to adsorb onto Fe oxyhydroxides from porewaters in oxic lake sediments (Tessier *et al.*, 1895)

In the Niagara river Murdoch and Duncan (1986) showed that Al, K and P increased with decreasing particle size due to their association with clay and together with Na, Ca and Ti were affected by local geological inputs. Cr, Co, V, Pb, Zn and Cu showed similar patterns of increasing concentration with decreasing particle size either due to being adsorbed on to Fe or clay particles.

Davenport (1990) found a number of controls on metal behaviour in stream sediments, including chemical and biochemical processes in the sediments, sorption to clay, co-precipitation with Fe/Mn oxyhydroxides and the behaviour of microorganisms. Hg was controlled by organic matter content. Fe and Mn correlated positively with Co and V.

The most important process in the behaviour of metals in lake sediments is the interaction with Fe, Mn and organic matter, with each of these in competition with the others to provide binding sites for the metals and their success being based on their relative abundance to each other (Luoma and Bryan, 1981). Absorption of Cu, Pb and Zn by the humic fraction has been shown to be more important in low iron oxide conditions (Luoma and Bryan, 1981) and the same study found that extractable Fe was more important than total Fe for binding Cd. The association the metals have with these components affects their bioavailability to organisms, e.g. Ag associated with Mn oxides is 100 times more available to organisms than when it is associated with Fe oxides or organic matter (Luoma and Jenne, 1977).

Tessier *et al.* (1989) found that less Zn adsorbs onto Fe oxides in acidified lakes. Pb is more likely to be scavenged by Al precipitates in acid lakes (Bendell-Young *et al.*,

1989), whilst Cd scavenging from lake waters is due to coprecipitation with or adsorption onto Mn oxides. Young and Harvey found that Zn and Ni adsorption was affected by pH and they were recovered mostly from the reducible fraction, whilst Cu was not (possibly as it was more likely to be bonded with organic matter).

A study of Loch Dee in Scotland showed an increase in Zn, Cu and Pb in the top 15cm reflecting industrial pollution input to the lake. Below 15cm there was little evidence of pollution input or diagenetic remobilisation. Fe, Mg, Cu, Cd, Co, Pb, and Ni were found mainly in organic complexes or as detrital silicates, whilst Mn, Ca and Zn were adsorbed or in the reducible oxide phases. In the contaminated zone, Pb was present as labile oxides or in the organic Pb phase (Williams, 1993).

During laboratory experiments on sediments from Esthewaite water, Hamilton-Taylor *et al.* (1996) found the important factors controlling Cu and Zn behaviour at the sediment water interface were mixing in the water column, sulphide precipitation in the sediments and anoxic hypolimnion and recycling from freshly deposited particles.

Lee *et al.* (1997) showed that metals in a retention pond beside a motorway in France behaved in a similar fashion to those in lake sediments, being partially controlled by diagenetic processes. Cd was enriched in the surface sediment (due to an increase in the loosely bound fraction from surface runoff) but lower down the core it was fairly constant. Zn, Mn and organic carbon decreased with depth whilst Pb and Fe were fairly constant with depth. It was thought that surface enrichment of Zn and Pb was due to their release from the sediment by early diagenetic reactions.

In benthic anoxic conditions Shaller *et al.* (1997) found that V, Cr and As had strong correlations with Fe, suggesting that authigenic iron oxides where important carriers of these metal in oxic conditions. In oxic waters V is usually present as a vanadate oxoanion (which has a tendency to form complexes with Fe), whilst in moderate reducing conditions the vanadyl cation is found. Chromium in oxic environments is usually present as a chromate ion which is weakly adsorbed to Fe oxides. The dominant form of As in oxic conditions is arsenate which is reduced to arsenite in

reducing conditions and will form arsenite sulphide in the presence of FeS. K concentrations in sediment can be influence by the use of fertilizers locally.

When comparing the behaviour of P in an oligotrophic and a eutrophic lake Gonsiorczyk *et al.* (1998) found Fe and Mn bound P was an important mechanism of release in the oligotrophic system, whilst in the eutrophic lake labile organic bound P was more important. In eutrophic lakes P coprecipitates with calcite which contributes to its permanent burial. Amounts of dissolved loosely adsorbed metal oxide and calcium carbonate bound P were higher in the eutrophic lake.

Construction in a local area can increase sediment yield to a lake (Charlesworth and Foster, 1999). Zn concentrations can be increased by increased traffic in a location (Zn is associated with tyre wear and tear) and can also be associated with a Pb increase from petrol usage. Pb in the atmosphere fell by approximately 77% after the introduction of Pb free petrol in the 1980s. Urban lakes can be a valuable method of investigating historic pollution inputs to a location (Charlesworth and Foster, 1999).

Kolak *et al.* (1999) found that in Lake Superior Cu was preferentially found in the organic fraction and that Cu concentrations were greater in nearshore sediments than in offshore sediments. Correlations with organic matter were much stronger at the offshore location suggesting that, in nearshore sediment, pollution input from mining was the major controlling factor in the behaviour of Cu, whilst in offshore sediments organic matter was a more important issue.

In a lake undergoing rapid sedimentation, sediment layers maybe isolated from the water column before early diagenesis can occur. Diagenesis may be limited by the supply of organic matter which results in a rate too slow to alter the sediment geochemistry and trace metal profiles, which can make these sediments a good record of the pollutant input to the system (Callendar, 2000).

Tessier (1985) demonstrated in low pH Cd, Cu and Zn were much more likely to be partitioned to Fe oxyhydroxides than to be present in the porewater.

A study by Charlesworth and Lee (2001) showed in urban lakes that trying to match up sediment cores using SIRM and χlf can be difficult due to the variability of pollution sources within these areas. They found that even within the same lake the depth of related magnetic properties can vary, making it difficult to match up cores.

In lake sediment a number of elements experience a change in redox potential and solubility (As, Co, Cr, Fe, Mn and v) and will migrate with changing redox potential. Other elements are less mobile (Cd, Cu, Pb and Zn). Metal sulphides form under reducing conditions and these have extremely limited mobility within the sediments. The slow reaction rates of Fe and Mn oxyhydroxides mean that any metals released by these are often reabsorbed before they can be remobilised through the sediment. It was suggested that peaks in Pb, Zn Cd and Cu in areas of very low sedimentation rate would occur under the peak in Fe and Mn (Boyle, 2001).

Yang *et al.* (2001) showed that a single sediment core is unlikely to be able to be used to adequately represent the pollution history of a lake, due to within lake fluctuations in sedimentation rates and metal distribution. A decrease in Hg concentration corresponding to low organic matter can indicate dilution by mineral particles. Plant debris in sediment appears to have a strong tenancy to adsorb Hg.

Sediment focusing is a process whereby fine grained sediment is redistributed from areas of erosion (usually nearshore) to depositional areas by storm events and lateral currents. If there are pollutants associated with this sediment these will be redistributed as well, and this can lead to higher concentrations in depositional parts of the lake. This can lead to the false impression of elevated pollution levels in certain areas (Davis & Ford 1982; Eisenreich *et al.*, 1998). Sediment focusing usually affects large lakes with strong currents or those with localised inputs and can lead to an uneven distribution of sediments, with the most deposition occurring in the deepest part of the lake (Lehman, 1975). There are a number of other processes that can affect sediment distribution and settling in lakes including: river delta formation (coarser sediment settles out as the river enters the lake); river plume sedimentation (the settling out of finer particles as the river flows further into the lake); continuous complex mixing (on-going mixing of settling sediment); intermittent complex mixing (intermittent resuspension and redistribution of sediment); peripheral wave attack;

current erosion and redeposition: slumping and sliding on slopes; organic material degradation (Hilton *et al.*, 1986)

2.3 Organic Pollutants

The first PCBs were commercially manufactured in the USA in 1929. Their use increased rapidly as did their worldwide production which peaked in the 1960s. PCBs were first detected in the environment in 1966 by Jensen (1966). These substances are very resistant to degradation and therefore remain in the sediment for many years after production and emissions have ceased. PCBs are used in transformers, capacitors, hydraulic fluids, lubricants, plasticizers, dyes, adhesives. By the mid to late 1970s concerns about their ecological impact had led to restrictions being placed on their use and manufacture by governments in both Europe and the USA. In the USA their use was restricted to closed electrical systems in 1971 and then production was banned in 1977 (Valette-Silver, 1993). PCBs can enter the environment from landfill sites, incineration and industry. Scrimshaw *et al.* (1994 and 1996) have shown that stable organochlorines are a very damaging and very persistent form of pollution.

Acceptance of the potential dangers to the aquatic environment associated with organochlorines started in the 1960s with the problems caused by the accumulation of DDT in the tissues of aquatic organisms such as seals and fish. However, it was not until the development of a process that was exceptionally sensitive to organochlorines (Gas chromatography and electron capture devices) that measurement of levels of these chemicals could be routinely carried out. This technique allowed the identification of DDT in Antarctic organisms, which led to the identification of the process of atmospheric transport of organochlorines distributing them all over the world (Holden, 1981). PCBs are now a global pollution problem, having been detected at every site they were tested for.

PCBs bind to organic matter in sediments and soils and, once they enter the food chain, they accumulate in fatty tissues. To date PCBs have been found in samples analysed from all over the world. This is due to their being carried *via* an

atmospheric transport system to all corners of the earth (Alcock *et al.*, 1994). One of the main reasons for concern about PCBs in the marine environment is their persistency and stability. They are lipophilic in nature and therefore will become stored in tissue with a high lipid concentration. High concentrations are often found in animals that have a high fat or blubber content, for example, whales and seals. These high levels have been linked with reproductive disorders and lowered resistance to disease (Morris *et al.*, 1989; Law *et al.*, 1991). Camacho-Ibar (1996) showed PCB levels in benthic crabs from Liverpool Bay at up to 36 times higher than in the sediments, indicating that they were bioaccumulating and, therefore, could be a threat to human health if they entered the food chain.

It is important then that a record of the PCBs entering (and those already stored in) the environment be obtained. Law *et al.* (1991) looked at the PCBs suspected to be entering a site near Wrexham, North Wales and found that levels of contamination decreased moving downstream from the discharge site. Very low concentrations were found in fine sediment at West Kirby and this ties in with work done in the River Seine in France (Abarnou, 1987) that showed that the distribution of PCBs was linked to the dispersion of fine sediment particles on to which the hydrophobic PCBs became adsorbed. Law *et al.* (1991) stated that in this case it was unlikely that any significant amounts entered the marine environment *via* the river and that any inputs most likely came from direct discharge to the sea or atmospheric sources (Alcock *et al.*, 1994).

The 209 PCB congeners are produced by the chlorination of biphenyls. The naming of each of the congeners is related to its pattern of chlorine substitution (IUPAC numbering system) and this controls the congener's behaviour in the environment and its toxicity.

The lower chlorinated PCBs can be broken down aerobically by micro-organisms and the higher chlorinated ones, in many cases, can be broken down by anaerobic processes by the removal of *m*- and *p*-chlorines. This leads to an increase in the levels of lower chlorinated PCBs. Dechlorination rates are higher at lower PCB concentrations and can be limited by the presence of certain nutrients (e.g. vitamin B_{12}) within the sediment and can be increased by the presences of trace metals such

as $Zn^{(II)}$, $Cu^{(II)}$, $Ni^{(II)}$ and $B^{(II)}$ (Abramowicz *et al.*, 1993). Van Dort *et al.* (1997) have shown that PCBs degrade slowly within the environment, often over many decades and they can be dechlorinated by microbes. Those with more than 5 chlorine atoms are often not easily broken down by microorganisms and therefore are much more persistent. These are also more likely to bioaccumulate due to their higher octanol water partition coefficients. The PCBs with the highest toxicity are the congeners with chlorine in the mono-*ortho* or non-*ortho* positions (Van den Berg *et al.*, 1998).

Factors affecting the degradation of congeners include: the composition of the original parent mixture; site specific factors such as source of the PCBs; the medium involved (water, air or soil) and its physical characteristics, e.g. temperature, pH, particle size and organic matter content (Martin *et al.*, 2003).

The onset of the manufacture and use of various chemicals can be used a method of proxy aging of sediments, e.g. PCBs and DDT. If a long enough core is taken it may be possible to identify background (natural levels) of metals and then see an increase related to the onset of the industrialisation of an area and use that as a method of aging of a core and in establishing the sedimentation rate from the location the core was taken from (Fox *et al.*, 1999).

The relationship between organic matter and PCB content of the sediment is due to the organic matter acting as a substrate for the hydrophobic organic contaminants to adsorb onto. PCBs can, however, also be associated with coarse particles (Lohse, 1991). Preston and Raymundo (1993) and Tyler *et al.* (1994) suggest that adsorption of organic compounds is controlled by the apolar lipid content of the particles. Brownawell and Farrington (1986); Baker *et al.* (1986) and Lara and Ernst (1990) have all shown PCBs have a preferential adsorption on to organic matter within the sediment. However, if there is large amount of fine sediment present in a sample, then this could lead to the over estimation of the amount of PCBs in an area and if large amount of coarser grained sediment was present it could lead to the under reporting of contamination levels.

Thompson *et al.* (1996) showed that PCB concentrations were higher in sediments consisting of fine, silty mud and lowest in coarser, sandy sediments. It is possible

that Total Organic Carbon controls the amount of PCBs found in sediments but in this case there was only a weak correlation between these two parameters. Correlation was higher if the coarser fractions were removed from the analysis, suggesting that PCBs are found associated with organic-rich, fine grained sediments. Ko and Baker (1995) also observed PCBs tendency to partition to finer grained sediments. Pierard *et al.* (1996) found an association between low chlorinated PCBs and sand-sized fractions (>63 μm) and high chlorinated PCBs and silt-sized fractions (<63 μm). Interactions with sediment are related to organic matter content, nature of the surface and the surface area. Therefore, in sediment they are found particularly on clays and fine particles with high surface to volume ratio and high organic matter content. Small particles have increased sorbption capabilities due to larger surface area / volume. Edgar *et al.* (2003) showed that the concentration of some congeners increased with grain size, some decreased and others have no relationship.

Due to their hydrophobic, particle-associated behaviour one of the important factors controlling the presence of PCBs in wetland environments is the sedimentary deposition pattern. If there is a large amount of sediment settling out from the water column then the levels of PCBs in the sedimentary record will be higher. It follows then that in areas of calmer water there will be higher rates of sedimentation and therefore higher levels of PCBs present. In areas of high bioturbation there will be more transportation of pollutants (and sediment) from deeper in the sediment to shallower areas leading to confusion of the deposition history. So sampling should ideally be done in areas with high sedimentation and low bioturbation. Sedimentary records can be lost during periods of resuspension caused by turbulence (possibly due to higher water input in wet years) or dredging of an area. However, in areas of very high sedimentation rates it can be quite difficult to sample for historical contaminants as the core lengths needed may be fairly long. Latimer *et al.* (1996) found that there was no overall trend of declining PCB levels in recent years. Monitoring of pollutant inputs can be used to calculate rates of sedimentation if the core samples can be correlated with certain pollution events such as the onset of PCB production or a major release incident. The proximity to the pollutant discharge will also govern how much enters the sedimentation process. The work in this paper also suggested that the water column maybe a significant source of PCB pollution to the

atmosphere (Latimer *et al.*, 1996). The more water soluble low chlorinated PCBs are likely to be transported further from the source than the higher chlorinated PCBs.

Chang *et al.* (2001) and Gil and Vale (2001) have shown that increases in low chlorinated PCBs with depth can be associated with dechlorination over time due to diagenetic processes. Sediments close to the surface that contain high concentrations of low chlorinated PCBs would not have had time for this process to occur, as it is a slow process (Natarajan *et al.*, 1998). Therefore, the mineralogy should be investigated as, if this shows changes in the nature of the deposits the concentration of PCBs is more likely related to that than diagenesis. Lee *et al.* (2001) suggest in summer photodegredation of exposed surfaces can breakdown the more highly chlorinated PCBs to lower chlorinated PCBs.

Ko *et al.* (2003) observed that tidal currents and storms provided an influx of energy to aid in the process of physical resuspension of sediments and led to the extension of their residence time in the water column. This, in turn, can lead to the release of the organic contaminants attached to these particles and these contaminants may be resuspended and settle out many times before degrading or being buried.

Organochlorine pollution can be measured using sediment cores to give an overview of input from both local and global sources. Barra *et al.* (2004) looked at organochlorine levels in sediment in conjunction with ^{137}Cs dating to investigate pollution levels over time in sediments in Chile. Levels in Chile were less than in comparable areas of the northern hemisphere, but on a par with those found in pristine areas of the northern hemisphere (Columbo *et al.*, 1990; Prats *et al.*, 1992; Muir *et al.*, 1996). Higher levels of penta- to hexa-chlorinated PCBs were found indicating a local source. PCB concentration was found to have increased in recent years, probably due to their usage in transformers etc.

Larsson and Sodergren (1987) undertook as series of experiments to try to determine the relative importance of various processes in the transfer of PCBs from the water column to the sediment and *vice versa*. They used a mesocosm approach in which two large tanks of freshwater, with a bottom layer of lacustrine sediment were used to represent the aquatic environment and the rate of release of PCBs to water, air and

aquatic organism (eels *Anguilla anguilla*) was measured. It was found the major flux was between sediment and water with a lesser amount being transferred to the air. This was found to relate to water temperature, with higher levels being transferred from the sediment in warmer temperatures (20°C). Sedimentation of PCBs was greater in the autumn than the flux from the sediment to the water and air. This is due to the release rate of PCBs from sediment being related to solubility. As temperature increases, so does solubility, therefore more PCBs are released from the sediment to the water. Low temperatures also lead to lower activity in benthic organisms and therefore lower rates of bioturbation. Microbial activity decreases as temperature decreases, leading to lower rates of mineralisation and gas production. There are fewer phytoplankton in colder months, so less lipid store to hold the PCBs. The more particulate matter there is in a location the higher the transfer of PCBs to the sediment will be. This is because the PCBs adsorb to the particulate matter which eventually settles out and becomes incorporated into the sediment. So a water body with a high level of phytoplankton will have a larger rate of transfer of PCBs to the sediment than one with fewer phytoplankton. PCBs entered the fatty tissues of fish *via* uptake from water, sediment, particulate matter and food. Algal mats covering the sediment can also reduce the amount of PCBs entering the water column from the sediment as they adsorb them. If these mats are a food source for aquatic organisms then they can provide a route into the food chain for the PCBs. However if sedimentation of particulate organic matter is very high in summer it can affect the overall flux of PCBs from the sediment to the water column. Transfer from the water to the air was higher in warmer temperatures as compounds leave the water by a process of volatilisation and it has been shown that less chlorinated PCBs volatilise faster than more chlorinated ones. PCBs in a gaseous state will remain in the atmosphere (and hence be transported further) than those associated with particles (Larsson and Sodergren (1987).

Another factor that can affect the concentrations of PCB congeners is changes in the source of the PCBs, with different mixtures entering the environment over time. There will also be selective redistribution of certain congeners within the sediment. For example, the less chlorinated congeners are more aqueous soluble and more likely to volatilise and, therefore, to be redistributed to shallower sediment. There will also be selective destruction and transformation of those that are present. In

some cases PCBs have been found in sediments that predate PCB production. Reasons for this could include downward migration of the PCBs, mixing of the sediment by bioturbation, contamination of the samples in the sampling or analysis phases, and even incorrect dating of the core samples (Gevao *et al.,* 1997).

The most toxic of the PCBs are the coplanar congeners such as 3,3',4,4'-tetrachlorobiphenyl and 3,3',4,4',5-pentachlorobiphenyl (McKinney *et al*, 1996; Poland and Glover, 1997) which are highly persistent. Levels of these have been found in killer whales, porpoises, Forster's tern eggs, dogs, cats and humans. It seems that higher levels are found in marine mammals than in those of terrestrial origin due to their lower capacity to metabolise them and it would appear that ability to metabolise them is dependent on the positions of the chlorine atoms. There needs to be at least one ring of biphenyl with adjacent nonchlorinate *meta* and *ortho* carbons (Tanabe *et al.,* 1987).

Kannan *et al.* (1989a) have shown that no enrichment of co-planar PCBs occurs in sediments, they just accumulated whatever was discharged in proportions relative to their presence in the environment. However, some of the most toxic, co-planar PCBs, e.g. 3,3',4,4',5-P_5CB will accumulate more readily, and have a longer half life (13 days as opposed to 6 days) in the tissues of certain organisms (e.g. the mussel, *P. Viridis*) than other pentachlorobiphenyls (Kannan *et al.*, 1989a,b,c; Tanabe *et al.*, 1987).

PAHs found in the environment come from a variety of sources, some natural and some synthetic; including volcanoes, forest fires, vehicle emissions, industrial releases, oil spills and waste incineration (Yunker *et al.*, 2002). They can be produced naturally *via* diagenesis from organic matter (Benlahcen *et al.*, 1997). They usually occur as mixtures which can, in some circumstances, be used as a method of identifying their source (Law and Biscaya, 1994). They adsorb onto sediment and organic matter particles, but undergo weathering and biodegradation which can complicate the task of source apportionment. The main cause of redistribution of PAHs is particle resuspension (Latimer *et al.*, 1999). Like PCBs they are persistent and can often be found in high concentrations associated with fine grained sediments and organic matter (Witt, 1995; Xia and Wang, 2008). Due to volatalisation, the

concentrations of the lower molecular weight PAHs are often lower than those of the higher molecular weight ones. Once in the sediment they can be broken down by bacteria (Rothermich *at al.*, 2002; Lei *et al.*, 2005).

2.4 Chapter Summary

This chapter shows the number of factors that influence the behaviour of metals and organic pollutants in saltmarsh, estuary and lake environments. In saltmarshes, sediments are trapped by vegetation leading to the development of the marsh and these same sediments can accumulate pollutants leading to the development of a pollution history for the region within the sediment record. This is particularly important in environments near industrialized estuaries.

The main sources of metals to wetland environments are natural processes (geological weathering and biological decomposition), material brought in *via* the tide, land runoff, atmospheric fallout and biological productivity and, anthropogenic inputs from human activities such as mining, industrial ore processing, sewage, waste runoff and incineration. Spatial fluctuations will be related to sources of emissions, mixing and temporal controls such as increased water flow and season production of phytoplankton.

A number of physical processes affect the sediment build up in both estuaries and lakes. Bioturbation, wave action, and human disturbance (dredging) can remobilise and re-oxygenise sediments. This can lead to movement of pollutants within the sediment and also the release of these pollutants from the sediment and redeposition elsewhere. Pollutants are often found preferentially attached to the finer grain sizes and sediments rich in organic matter. Temperature will affect microbial activity in the sediment and can therefore speed up (higher temperatures) or slow down (lower temperatures) biodegradation and bacterial activity.

Chemical processes within the sediment also influence the behaviour of metals and POPs. Diagenetic processes control the behaviour of the metals, e.g. pH, redox conditions, organic matter content and sediment composition and can lead to

remobilisation, removal or redeposition of these substances elsewhere within the sediment record. Because of their lower buffering capacity, lake sediments are much more sensitive to acidification processes than estuarine sediments and this can affect the concentrations of Transition metals (e.g. Al) within them.

Localised sediment composition and post-depositional regime can sometimes make it difficult to distinguish between anthropogenic and natural sources of metals and POPs. An increase in the concentration of lower chlorinated PCBs with sediment depth may not be related to pollution input but actually be due to anaerobic bacterial breakdown of the higher chlorinated congeners.

CHAPTER 3

POLLUTION AND THE MERSEY BASIN

This chapter examines pollution and the Mersey Basin. A consideration is given to the factors affecting sediment and pollutant transport and behaviour in the estuary, the variety of habitats and land use in the Mersey Basin and the industrial history and sources of pollution to the region.

3.1 The Mersey Basin and Mersey Estuary

The Mersey estuary has in the past been one of the most polluted in Europe. The estuary, saltmarshes and local wetlands, due to their proximity to large industrial/urban areas, have been the end point for a variety of man-made pollutants, including heavy metals and organochlorines, for the last 200 years (Fox *et al.*, 1999; Fox *et al.*, 2001).

The Mersey Basin is located on the northwest coast of England. It encompasses St Helens and Stalybridge in the north and north east, the Pennine fringe (between Manchester and the Pennines in the east and Stockport and Ellesmere Port in the South (Tomlinson, 1997) and includes most of the catchments of the Rivers Mersey and Irwell. Any study looking at the Mersey Basin must also take into consideration the influence of factors in the Liverpool Bay area. This is an area that covers three counties (Lancashire, Merseyside and Cheshire) and stretches from Rossall Point, Fleetwood (Lancashire) in the north to the Welsh border of the Dee Estuary in the south. It includes the estuaries of the Dee, Mersey, Alt and Ribble and a range of coastal habitats such as saltmarshes, sand dunes and soft cliffs (George, 1997).

The river Mersey forms at Stockport, where the rivers Tame and Goyt merge, and flows into the Irish Sea *via* the Mersey estuary (Figure 13). The estuary is 47 km long, from its tidal limit at Howley Weir to its mouth at New Brighton, and has the second largest tidal range in the UK (mean 8.4 m), with current velocities of up to 3.0 ms^{-1}. The drainage area is approximately 5000 km^2 (Martino *et al.*, 2002). The estuary can be divided into four main sections, the Upper estuary, the Inner estuary, the Narrows and the Outer estuary (NRA 1995).

The upper estuary is a narrow channel located between Warrington and Runcorn. The Inner estuary is a large basin starting just below the Runcorn Gap. On its southern shore it has an extensive saltmarsh system and supports a bird population of national significance. The Narrows are an area where the channel becomes straight and narrow downstream from the Inner estuary. They are deep (up to 30 m at low tide) and have a high current speed (6 knots). The Outer estuary is a large area of intertidal sand and mud banks with the Crosby and Queens's channels maintained by dredging (NRA 1995).

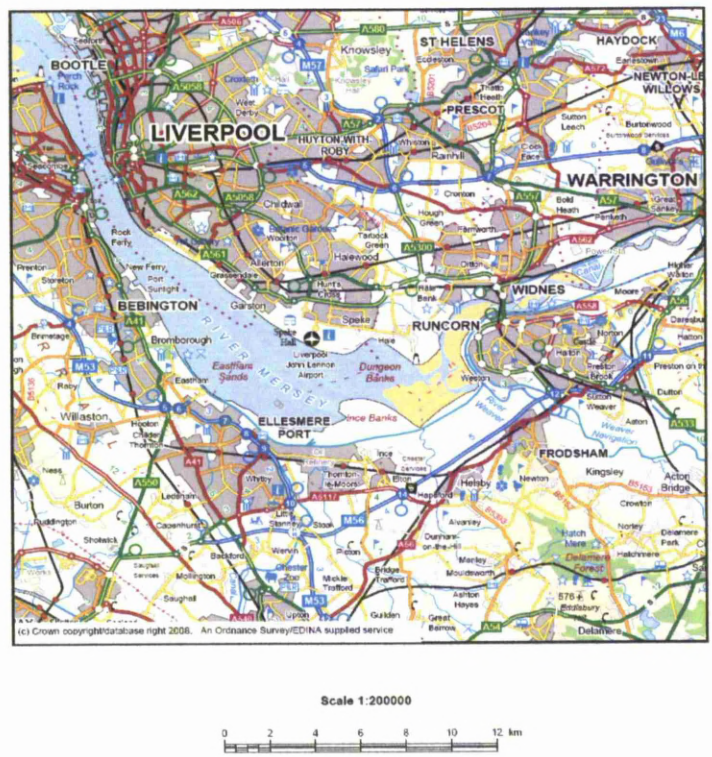


Figure 3: The Mersey Estuary.

Due to its unusual 'bottle neck' shape (widening from 1 km at Widnes to 5 km at Hale and back to 1 km at New Brighton) the Mersey is an extremely dynamic system. The high tidal velocities lead to scouring of the channels and continual resuspension and remobilisation of sediments and particulate matter. This, in turn, leads to the high turbidity found in the water (over 2000 ppm near Runcorn bridge) (NRA 1995). Much of this is alluvial sand and silts from upstream (although some is of marine origin). The highest levels of pollution are detected in the Upper estuary,

due to the reduced amount of dilution taking place, as only flood tides reach that far upstream (NRA 1995).

Water quality in the estuary ranges from Class D (bad) in the Upper estuary to Class C (poor) in the Inner estuary and Narrows to Class B (fair) in the Outer estuary. As a result of improved sewage treatment in the area, BOD (Biological Oxygen Demand) in the estuary has declined and the result of this is that oxygen levels within the water have increased (although there are still areas of very low oxygen) (Harland *et al.*, 2000).

3.2 Sediment Sources, Transport Pathways and Processes

The particulate matter that eventually forms the sediments in the estuary comes either *via* marine input from the Liverpool Bay or from alluvial silts and clays brought downstream by the river Mersey. The Mersey estuary is gradually accreting sediment (coarse sand from Liverpool Bay and finer materials from upstream). The finer particles either settle out in areas of very low flow or are transported by the current to the Irish Sea. The majority of resuspension occurs during spring tides in the shallow areas of the estuary (NRA 1995). Both these processes contribute to the constantly changing position of the low water channel and the build up or erosion of the estuary's saltmarshes, which in turn leads to the storage or release of pollutants within the sediment (NRA, 1995).

There is an overall movement of sediment (particularly sandy sediment) into the Mersey estuary from Liverpool Bay (O'Connor, 1987; Thomas *et al.*, 2002), encouraged by onshore currents near the sea bed (Ramster and Hill, 1969). This seems to have been enhanced in recent years by the construction of training walls (1909 to 1949) and dredging operations in the outer estuary (Thomas *et al.*, 2002; Blott *et al.*, 2006). In 1906 there were three main channels in the inner estuary and between 1906 and 1936 these became more defined. The main channel in the eastern part of the inner estuary had migrated northwards causing significant erosion of the Dungeon Bank and accretion of the Ince and Stanlow Banks on the southern side of the estuary. There was a deepening of the eastern side of the Eastham channel and a

narrowing of the Gartson channel. Between 1936 and 1956 there were only minor changes to the estuary, with the Eastham and Ince Banks continuing to accrete. By 1977 the southwards migration of the main channel had allowed accretion to occur at Dungeon Banks and erosion of the north side of Ince and Stanlow Banks. Between 1977 and 1997 Eastham Sands had been subjected to significant erosion. However, during this time Stanlow Bank continued to accrete, the Gartson channel had deepened (possibly encouraged by dredging operations) and the Middle Deep had infilled somewhat. Between 1906 and 1997 the overall volume of sediment in the inner estuary increased, particularly between 1936 and 1956 and corresponding to the reduction in dredging during WWII (Blott *et al.*, 2006).

The amount of sediment brought downstream by the river has always been relatively small in comparison to that entering from the Irish sea and the fluvial supply was further reduced following the building of the Manchester Ship Canal in the 1890s (Comber *et al.*, 1993). Sediment accretion rates are thought to be approximately 3% of the ebb/flood sediment exchange (~1 million cubic metres per year) (Lane and Prandle, 2006). Lane (2004) modelled sediment fluxes in the Mersey and showed that they are dominated by fine sediment (silt) movement on the Spring tide and that there is relatively little contribution to the sediment regime by river flow, saline intrusion or dredging.

Factors affecting the supply and movement of sediment to the Mersey Basin include sea-level change, tidal regime, storm surges, grain size distribution, anthropogenic factors such as dredging, port development, land reclamation and development and coastal defence construction (Thomas *et al.*, 2002; Blott *et al.*, 2006; Pye and Blott, 2008). Erosion of soft cliffs in areas like Garston and Widnes and unconsolidated quaternary sediments north of Crosby also provide a sediment input to the estuary (Blott *et al.*, 2006).

There is some evidence to indicate that the inner estuary has become less flood tide dominant (particularly in the period between 1956 and 1977) (Thomas, 1999), but Lane (2004) concluded that this had no long term effect on the estuary. The effects of wind conditions, in general, on the sedimentary environment of the estuary are

poorly understood, but Pye (1991) indicates that individual storm events can contribute to resuspension and redistribution of sediments within the estuary.

When compared to other estuaries (Dee and Ribble), in the Mersey estuary there has been only a relatively small amount of land reclamation. This is mainly concentrated around the Liverpool and Seaforth Docks and the Ince Banks area affected by the construction of the Manchester Ship Canal, and it is thought that the effects on the sedimentary regime have been fairly small (O'Connor, 1997). There is a salinity gradient in the estuary from the upper limit at Howley Weir to the Irish Sea, this varies with freshwater flow and tidal currents (Hartnett and Berry, 2010) which will affect the behaviour of sediment bound pollutants.

Due to the tidal dynamics in the estuary (strong tides and currents) resuspension, redistribution and resettlement of bed sediments occurs frequently (Hartnett and Berry, 2010). This will affect the concentration of suspended particulate matter in the water column and lead to a complicated pattern of sediment (and therefore sediment bound pollutant) movement round the estuary. Cohesive sediment (which binds heavy metals) is predominantly found in the area from Runcorn seawards with non-cohesive sediments (those that are less successful at binding metals) found mainly in the area from Howley Weir to Runcorn (Hartnett and Berry, 2010). Suspended sediment load increases with the onset of the flood tide and decreases as the tide ebbs. Currently the estuary is stable state although localised erosion and accretion may be occurring in certain areas (Thomas, 2002). Non-cohesive sediment transported *via* suspension and bedload accounts for the majority of the sediment entering the estuary. Sediment particle size tends to increase moving offshore (Kritsov *et al.,* 2008) but this is complicated by factors such as flocculation and aggregation caused by interaction with the biota, e.g. mucus production by plankton can increase flocculation.

The lower Mersey Basin catchment contains a number of industrialised areas Manchester, Bolton, Bury, Rochdale, Oldham, Stockport, Warrington, Widnes, Runcorn, St Helens, Ellesmere Port, Crewe, Tranmere and Liverpool, all of which will contribute a pollution load to the estuary making it difficult to identify specific sources of individual pollutants. The majority of freshwater entering the estuary

from rivers comes from the Mersey, the Manchester Ship Canal and the River Weaver (Harland *et al.*, 2000). The sediment supply to isolated lakes (e.g. Speke Hall) comes from either windblown deposition or overland runoff and will, therefore, have a tendency to be of finer particle size than those supplied to the estuary *via* river runoff and tidal input from the Liverpool Bay area.

PAHs from pyrolytic sources are often bound to ultra-fine super soot particles which can lead to them being transported great distances by the wind. These super soot particles have been shown by Gustafsson *et al.* (2001) to make up 2-30% of total organic carbon in coastal sediments

3.3 Habitats in the Mersey Basin and Liverpool Bay Area

As mentioned earlier there are four estuaries running into the Liverpool Bay area (The Alt, the Mersey, the Ribble and the Dee). They each have a large expanse of sand and mudflats and are backed by saltmarshes and sand dunes. They host migratory birds during spring and autumn and are important areas for waders and wildfowl and a number of shellfisheries, including cockles at Talacre, Salisbury bank, Thurstaston and West Kirby in the Dee. The Dee and the Ribble are also important rivers for trout and Salmon. A number of factors, both historical and current are influencing the environmental quality of the estuaries including, dredging (e.g. to keep shipping channels open), fishing, recreational usage, effluent disposal and reclamation of intertidal land (George, 1997; Tomlinson, 1997).

Sand dunes are primarily located along the Sefton coast but are also found on the Wirral and Fylde Coasts. Rich agricultural land (reclaimed from mossland) can be found behind the dune systems and a number of SSSI and NNRs (including Ainsdale NNR) indicate the importance of the area as a habitat for various protected species (Natterjack toads, Red squirrels and Great Crested newts, for example). There are a number of factors currently affecting the dune system: coastal defence can limited the supply of sediment for the dune system; erosion and destruction of vegetation can be a problem caused by recreational activities; invasive species such as sea

buckthorn can affect habitat composition, as can processes associated with urban development, e.g. laying of wastewater pipelines (George, 1997; Tomlinson, 1997).

Saltmarshes make up a large part of the Merseyside coastline and many of these include upper and mid marsh communities that have been lost in other parts of the country due to land reclamation. Since the 1920s there has been an increase in newly colonised saltmarsh areas due to the introduction of cord-grass, however in other areas erosion is removing saltmarsh habitats. Saltmarshes in the region provide an important habitat for a number of bird species including snipe and an overwintering location for species such as pink footed geese, whooper swans and teal (George, 1997; Tomlinson, 1997). There are a number of cliff habitats on the Mersey estuary including at Hale, Eastham and Hilbre island and these provide important habitats for a number of plant species (rock sea lavender and fern spleenwort) (George, 1997; Tomlinson, 1997).

Merseyside has a number of important lowland heath areas found on sandy hills that are home to important species such as sliver studded blue and grayling butterflies (George, 1997). Many of these areas on the Sefton coast have been incorporated into golf courses (Tomlinson, 1997). A lot of the lowland peat mossland has been drained for agricultural use or used for fuel and fertiliser. A few still remain (e.g. Risley Moss and Red Moss) and they are important as they preserve climate and land use change records (Tomlinson, 1997). Current pressures on them include the drainage of surrounding land for agricultural purposes, their use as tipping sites, recreational activities and eutrophication (Tomlinson, 1997).

A considerable amount of the Mersey Basin urban area is made up of lowland grassland. Much of this has undergone improvement for agricultural purposes. The grassland can be split into a number of types including: unimproved permanent grassland (often found on the edge of farmland); hay meadows; flood meadows and inundation grasslands; coastal grazing marshes (often including networks of brackish or freshwater ditches) and acid grasslands. These grassland areas provide habitats for a wide range of organisms including reed bunting, moorhen, snipe, lapwing, barn owl, pin tail and golden plover (Tomlinson, 1997). They are threatened by overgrazing (e.g. by horses), over-intensification of agriculture and development

(urban, suburban and industrial). Traditionally managed arable land makes up a small proportion of the land in the Mersey Basin. It is important as the traditional methods provide a valuable habitat for a range of species e.g. partridge, brown hare and skylark. Modern farming methods (e.g. pesticide use) keep the land more weed free, which is a threat to some of these species (Tomlinson, 1997).

About one fifth of the woodland in the Mersey Basin is Ancient semi-natural woodland. The largest concentrations are found on the Wirral and south eastern Greater Manchester. It is generally associated with narrow valleys cut by streams. It is often dominated by oak and sycamore with brambles, ferns and bluebells being common species found there. Alder is common in wetter locations. It is threatened by species invasion (himalayan balsam, rhodedendron), recreation pressure, fires and vandalism. There is also an area of ancient wood pasture at Dunham in Trafford that provides an important location for a variety of beetle species and the rare Black Poplar (Tomlinson, 1997). Four fifths of the woodland in the region is secondary and plantation woodland. It is important as it provides a wide range of habitats for a variety of communities (plants, birds, invertebrates) (Tomlinson, 1997).

Freshwater wetlands, canals, ponds and reservoirs provide a range of habitat types in the region. These have suffered from pollution inputs in the past but many have been cleaned up in recent years and now host a wide variety of species. Deeper lakes host diving birds such as grebes and coots, shallower lakes are preferred by ducks and moor hens. Canals provide a good location for freshwater sponges and damsel flies and the rare great crested newt can be found in ponds in the area. Restoration, recreation and development can negatively impact on the established communities (Tomlinson, 1997).

Due to the major conurbations in the Mersey Basin, urban areas provide an important range of habitats in the region. They include waste land, railways, parks, commons, gardens, disused buildings and former industrial sites (Tomlinson, 1997).

Other habitats in the coastal region include a number of man-made saline lagoons, some of which are brackis, plus a wide variety of other artificial habitats including groynes, docks and oil and gas platforms. Rocky shores are limited to a few locations

(e.g. Hilbre Island) and provide a habitat for animals such as mussels and barnacles and a variety of seaweeds. The majority of shores are sedimentary, comprised of sand and mud and species include those of bivalve molluscs and polychaete worms (George, 1997).

The seabed is a sedimentary environment made up predominantly of sand (coarse, fine and muddy), with pebbles and cobbles. The main factors affecting it are pollution, oil exploration, fishing, dredging and recreational activities (George, 1997).

The inshore/onshore water habitats contain a number of important fisheries including shrimp, plaice, whiting, brill, sole, rays and turbot. Some of these species also have their nurseries in the area (sole, plaice and rays). A colony of Grey seals can be found near Hilbre Island on the Dee. Environmental quality is affected by pollution (Mercury, PCBs and lead), litter (plastics and old fishing nets), fishing and recreational activities and oil exploration (George, 1997).

The area is used for a range of activities including; fishing, tourism, industry, oil and gas exploration, mining and mineral extraction, agriculture, urban development, dredging and nature conservation. Liverpool, Birkenhead, Lytham St Anne's, Southport and Blackpool in particular have high concentrations of residential and commercial land use and all these activities are contributory factors affecting the natural habitats (George, 1997).

3.4 Land Use in the Mersey Basin

The majority of the land in the Mersey Basin is agricultural (Figure 4). However, there are a number of urban areas which include the Liverpool city area and its surroundings (Rothwell *et al.*, 2010). These areas consist of a mix of residential and industrial land (Tomlinson, 1997). The Mersey Basin is one of the most densely populated areas in the UK, consisting of 2 major urban conurbations (Liverpool and Manchester), as well as a number of surrounding towns and cities including St

Helens, Warrington, Wigan, Halton, Birkenhead and Ellesmere Port (Tomlinson, 1997).

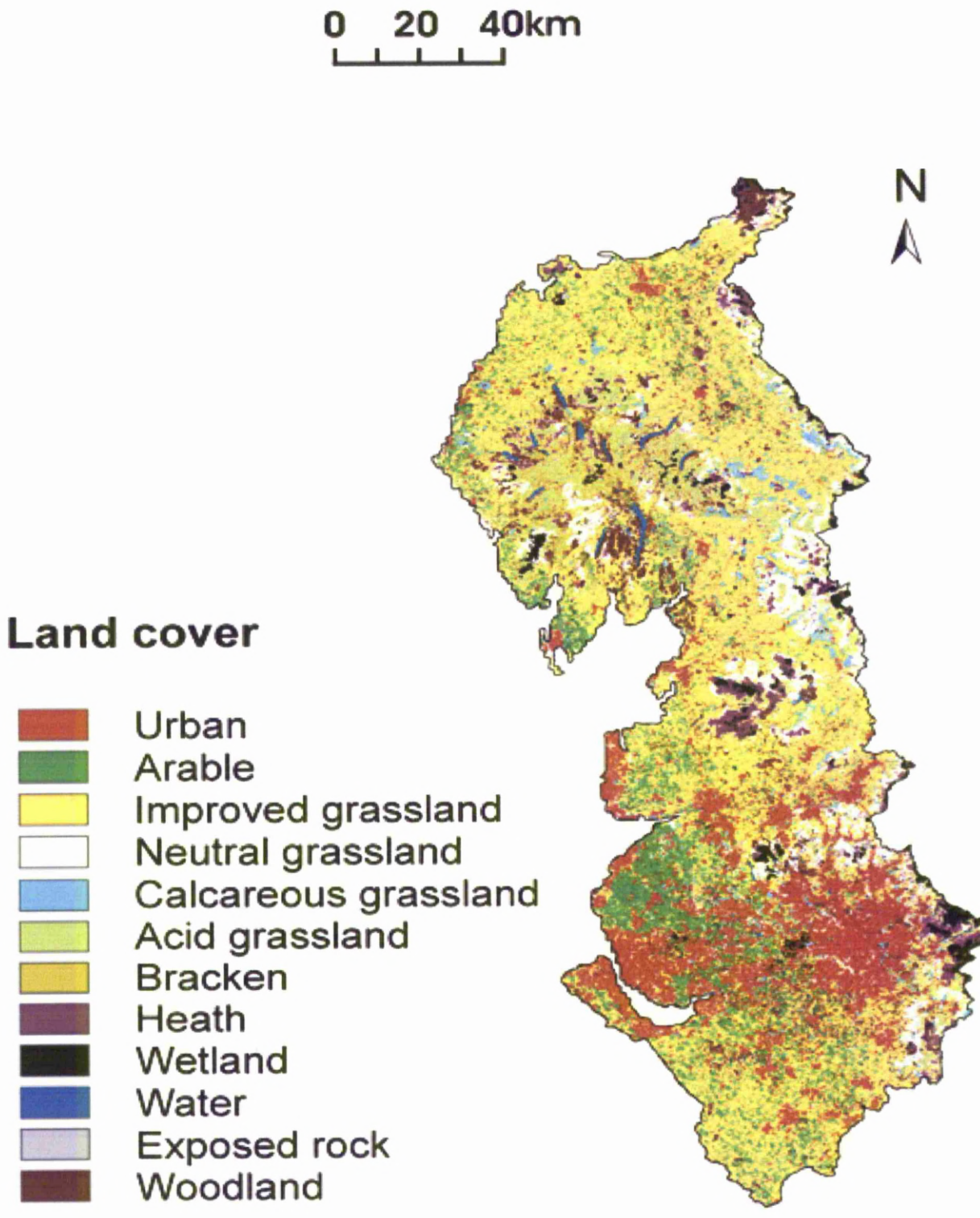


Figure 4: Map of Land use in North West England including the Mersey basin (taken from Rothwell et al., 2010).

The area in the north and north east corresponds to the edge of Lancashire coal measures and is characterised by gentle hills and valleys. In places the natural landscape has been modified by coal spoil heaps resulting from the historical mining activity in the area (Tomlinson, 1997). In the east of the basin close to the Pennines (and outside of the Manchester conurbation), the landscape consists of moorland, steep sided valleys and fast flowing rivers which contributed to the development of industry in the area. The majority of land is used for farming (permanent pasture) although some mineral extraction does still occur (Tomlinson, 1997). In the south (around Ellesmere Port and Stockport) there is a mixture of industrial development and arable land with some uncultivated peat mossland. Land use on the Wirral peninsula is a mix of lowland farming, small town urban developments and some industrial areas. The Liverpool conurbation consists of industrial and residential land (Tomlinson, 1997).

Following on from the industrial revolution in the 18th Century, there was a steady increase in both population density in the major towns and industrial activity in the Mersey Basin. A number of industries developed in the region (pottery, brewing, copper and brass making), particularly round the St Helens area. The extraction of coal increased in the Lancashire region and in the Pennines and all industries benefited from the construction of canals and later the railways, which also allowed the expansion of the textile industry.

By 1851 the Mersey Basin has become one of the world's most important manufacturing locations with 68% of the population living in urban areas. This level of urbanisation and industrial development led to loss of habitats (for housing, industry and agriculture) and an increase in aquatic and atmospheric pollution. A further period of urbanisation occurred post 1945 with the outward expansion of the suburbs due to the increase in car ownership. There was a general industrial decline in the region from the early 1920s until the 1960s when there was a move away from traditional industry such as chemical production to more high investment industries like electrical engineering, car and aircraft manufacturing. In recent years these industries have also faced decline due to global competition. Population increased up until around 1971, when levels stabilised. In the last thirty or so years, stricter

environmental legislation has allowed an improvement in the water quality and air quality in the region (Handley and Wood, 1999).

3.5 Industry, Pollution and the Mersey Basin

In the 15th Century the silting up of the river Dee led to the gradual increase in importance of the Mersey for trade purposes. This led to an increase in the population of the Liverpool area, from around 5,000 in 1700 to 223,000 in 1841. This rapid increase in population led to an increase in industry (on the estuary itself and upstream on the various tributaries) and, therefore, an increase in pollution (both from domestic and industrial sources) (NRA 1995). Industries that developed in the catchment area included cotton mills and the associated processes of bleaching and dyeing, including those companies manufacturing the raw materials, the paper industry and glass and heavy chemical industries round Widnes and St Helens. Shipbuilding and boiler making developed on the Wirral leading to a population increase from 110 in 1801 to 24,000 in 1851. Various other industries developed on the Wirral – soap making at Port Sunlight and oil refining and Stanlow. Similar population expansions were associated with the chemical industry in Widnes, Warrington and Runcorn (ICI) (NRA, 1995). The range of industry and land use in the region has lead to a variety of sources for pollution input (industrial discharges, agricultural runoff and sewage). Aquatic sources include direct discharges to rivers, lakes and estuaries, downstream transport from other parts of the region and remobilisation of pollutants stored in sediments. Atmospheric sources also contribute to the pollution load in the region and these include local industry and long range transport from other areas (Burton, 2003).

The Mersey drainage basin has a long association with the chemical industry dating back to the 19th century particularly with ammonia, sodium carbonate and chlorine production and use (Hardie, 1950). Other industries in the area include car manufacturing and oil refining. There are several ports (Birkenhead, Liverpool, and Ellesmere Port) located along the Mersey, as well as access to Manchester via the Manchester ship canal.

The association with organic chemicals started around the time of WWI (1914), with the production of chlorinated solvents and later (1930's and 1940's) the manufacture of pesticides such as DDT (dichlorodiphenyltrichloroethane), HCH (hexachlorocyclohexane), HCB (hexachlorobenzene). PCBs were never actually manufactured in the Merseyside area but were in use in the vicinity and have entered the estuarine system *via* atmospheric and drainage pathways (Fox *et al.,* 2001).

Commercial use of PCBs started in the UK in 1954, peaked between 1965-1975 (Gevao, 1997) and manufacture ceased in 1977. Fox *et al.* (2001) showed that PCBs appeared in Mersey estuary sediment from the late 1940s and peaked in 1970. However, even though production has ceased, levels in more recent sediment still remain high due to the persistence of these chemicals and the continued release from the equipment utilising them being discarded in landfill sites. Fox *et al.* (2001) found that except in recent sediments, penta- and hexachloro congeners were present in higher levels than tri-, tetra- and heptachloro congeners. Due to the long life of transformers is likely that PCBs will continue to enter the environment for some time.

In recent years there has been an increase in the use of the estuary and surrounding land for recreational and residential purposes (residential and tourist development at the Liverpool docks, including watersports areas) activities include golf, wild fowling, country parks, caravan and picnic areas and bird watching (6,700 hectares of the estuary are classed as SSSI and the estuary is internationally important for water fowl).

The Mersey Basin Campaign was established in 1985 to try to co-ordinate the cleanup of the Mersey (Burton, 2003). Work carried out over the last 25 years (Taylor, 1986; Harland *et al.,* 2000), on mercury and other metals (aluminium, lead, copper, nickel, and zinc to mention a few) has suggested an overall decrease in the levels found in surface sediment (except for aluminium) (Taylor, 1986; Harland *et al.,* 2000). This is likely to be due to stricter discharge regulations leading to improved effluent treatment by industry as well as change in operating practices within industry. BOD has been decreasing in recent years due to stricter discharge

controls and the diverting of sewage inputs, although in certain areas, under certain conditions there are still zero oxygen levels (Harland *et al.*, 2000).

Liverpool Bay has been regularly monitored for pollutant levels since the early 1970s, although the majority of these studies concentrated on trace metals and not on the organic pollutants (Norton *et al.*, 1984; Rowlett *et al.*, 1986). The Mersey estuary receives a large amount of untreated and treated sewage. Campbell *et al.* (1988) have shown that Zn pollution comes from domestic sewage and Ni from industrial sources in the Mersey Basin. It has been shown that the suspended particulate matter from sewage sludge is particularly effective at removing the metals Cu and Cd and to a lesser extent Cr and Zn. They also found Cd was present in the weakly bound exchangeable and carbonates phases which means that it can be easily released to the water column.

The chlor-alkali industry started in the Mersey in 1890s with the development of the process of brine electrolysis using a mercury electrode. This has lead to an increase in the input of mercury and chlorine to the estuary. This increased through the 1st World War which was followed by a recession in the chemical industry. However the 2nd World War increased the need for chemical manufacturing which continued to grow along with other industries in the area (e.g. petrochemicals) up to the mid-seventies (Fox *et al.*, 1999; Fox *et al.*, 2001).

Lead enters the estuary from a major lead alkyl plant at Ellesmere Port and can also be related to mining activity, car exhaust emissions and as fly ash from coal fired power stations. It can also be associated with the use of lead based paints, particularly for ships (as can Cu and Zn) It is possible to relate a peak in Pb to a peak in leaded petrol use and a decrease in levels often correlates with the phasing out of this (Valette-Silver, 1993; Velde *et al.*, 2003). Lead is one of the major contaminants emitted to the environment, with levels being detected in remote areas such as Antarctica (due to atmospheric transportation).

Copper can come from smelting as can As, Ni and Co. Local emissions often come from electroplating as well as chlorine-alkali plants and these can also contain Zn, Cu, As, Hg Cr and Cd. The first copper works in the area were established in St

Helens in the 1850s (Rees, 2007). The industry declined in the mid 1920s but showed a revival during WWII and the 1950s (Harland *et al.*, 2000). Since then, however, it has declined. An increase in Cu could indicate industrial use – e.g. in piping, treated lumber (Cu sulphate can be used as a fungicide and antibacterial agent) (Velde *et al.*, 2003).

Arsenic contamination in the Mersey is probably related to historical copper smelting using imported Cu from South America containing arsenopyrite. Pollution levels should have fallen to near background levels by now, as the historic source is no longer in use and any found is likely to be the result of disturbance of contaminated sediment. Arsenic has also entered the estuary from the glass production industry based at St Helens (Rees, 2007). Cu has also been used in the past to control plant pathogens. Zinc was used for galvanising, and motor vehicle paint. Its use declined from the 1950s (Fox *et al.*, 1999).

Turner (2000) showed significant Cr contamination in Mersey sediments but only moderate Cu pollution. Lower salinities favour the release of sediment bound Cr to the water column (Abu-Saba and Flegal, 1995; Coomber *et al.*, 1995). Hursthouse *et al.* (2003) found that there was a significant relationship between Fe (and therefore Fe sulphides controlled by redox reactions) and Cr within the sediment. They also found a link with Mn and organic matter, though neither of these were as important to Cr levels within the sediment as Fe.

Nickel can be released from paperworks, sewage treatment works and power stations. Metal inputs can be enhanced by local mining activities (Valette-Silver, 1993). One of the major sources to the Mersey was from a manufacturer of the catalyst Raney Ni, Production of this was ceased in 1989 and replace by Ni oxide manufacture until 1998. In recent years a small amount of Ni enters the Mersey from its use as a hydrogenation catalyst during the manufacture of edible oils (Martino *et al.*, 2004)

Other sources of metals include airborne particulates from factory chimneys, incinerators and the burning of fossil fuels. Hg has entered from the Chlor-alkali industry at Runcorn and Ellesmere Port (Airey and Jones 1982, Campbell *et al.*,

1986) and from domestic waste and other parts of the Mersey chemical industry (Craig and Morton, 1976).

Mining has taken place locally (Knowsley and St Helens) since the 17th century (Rees, 2007) and that has included the extraction of lead sulphide and zinc sulphide.

A number of other industries can be found in the area including oil refineries and car manufacturing plants (Hardie, 1950). Currently, there are over 200 chemical producing and using companies located in the area that are licensed to release waste to the local environment including heavy metals, PCBs, PAHs and a wide variety of other compounds.

3.6. Chapter Summary

Due to its location, morphology and the industrial history of the region (particularly regarding the chemical industry), the Mersey estuary was once one of the most polluted estuaries in Europe. The majority of sediment enters the estuary from the Irish Sea but there is also an amount that comes from upstream sources *via* the river Mersey. The supply of sediment to the estuary is influenced by a number of factors including; sea-level change, tidal regime, storm surges, grain size distribution, anthropogenic factors such as dredging, port development, land reclamation and development and coastal defence construction. The majority of freshwater comes from the river Mersey, the Manchester Ship Canal and the river Weaver. The sediment supply to isolated lakes (e.g. Speke Hall) comes from either windblown deposition or overland runoff.

The Mersey Basin has a number of habits associated with it (including mudflats, sand dunes, saltmarshes, cliffs, lowland heath, grassland, arable land, woodland, freshwater and saline wetlands, lakes and ponds). A number of factors, both historical and current influence the environmental quality of the estuary and lakes including dredging (e.g. to keep shipping channels open), fishing, recreational usage, effluent disposal and reclamation of land. The majority of land use is arable but there are a number of significant urban and industrial areas within the region including Liverpool, St Helens, Warrington, Wigan, Halton, Birkenhead and Ellesmere Port.

The increasing importance of the Mersey for trade purposes and an increase in the Liverpool population in the 15th Century led to the increase in industry in the region and an associated increase in pollution input to the sediment. The industrial history of the region includes chemical industries, shipbuilding, glass making, textiles (and associated bleaching and dyeing), oil and gas and mining, all of which have influenced the pollutant history of the area. More recently there has been an increase in the recreational use of the area and an associated pressure to clean up the region (the Mersey Basin Campaign). Pollution input has been dropping in recent years due to improvements in technology and stricter discharge regulations.

CHAPTER 4
MATERIALS AND METHODS

4.1 Site Description and sample collection

Sediment cores were collected from two sites in south Merseyside (Figure 5). The sites were chosen in an attempt to identify the primary pollutant pathways and to compare the relative contribution of different sources of pollution to the area. The major source of pollution input to the lake core was most likely be from atmospheric deposition, whilst that measured in the saltmarsh core was likely to be more of a combination of aquatic and atmospheric pollution.

Figure 5: Oglet Bay (red circle) and Speke Hall Lake (blue circle).

4.1.1 Sample Site 1: Oglet Bay

The Mersey Estuary has a large intertidal area consisting of mud and sand flats adjacent to areas of saltmarsh (Blott *et al.*, 2006). One of these saltmarsh areas is located at Oglet Bay (Figure 5 and 6) on the north bank of the Inner Mersey estuary at the estuary's widest point (5km wide). Fairhurst and Buxton (1982) described it as a narrow band of saltmarsh approximately 100m wide. Oglet Bay is a well defined, dynamic saltmarsh that is in a constant state of flux, with some areas subject to

erosion and others subject to deposition. A relocation of the low water channel in recent years has resulted in marked retreat of the saltmarsh through block and gully erosion. Due to its proximity to the industrial area of Liverpool, it is the end point for a variety of industrial pollutants, both from atmospheric and aquatic sources, which makes it a good site for investigation of historical pollutant releases in the Liverpool area.

Figure 6: Oglet Bay sampling site (Red circle = Upper Marsh Core. Yellow circle = Channel Core).

Three sediment cores were taken from Oglet Bay (Figure 6) in November 2001. Two of the cores were consecutive (depth-wise) from high on the saltmarsh (red circle) (Upper Marsh Core - total depth sampled = 67cm) while one was from lower down near the river channel (yellow circle) (Channel Core - depth sampled = 36cm). The cores were taken by manually driving 50cm long plastic tubes into the sediment and then digging them out. Once back in the laboratory the sediment was extruded from the tube and sliced into 1cm sections. These sections were subdivided into two separate samples; one placed into a foil covered petri dish (for organic pollutant analysis) and the other into plastic sample bags (for metal analysis).

4.1.2 Sample Site 2: Speke Hall Lake

Records of a residence on the site of Speke Hall go back to the Doomsday Survey of 1086 (Millington, 1947; Tibbles, 1983). There have been a number of houses on the

site including a timber framed house and a sandstone manor which was replaced by the start of the existing house in 1490 (Millington, 1947; Tibbles, 1983). The Lake (Figure 7), also known as 'Speke Dam' was said to have been the water supply for the hall before mains water was installed (Whatmore, 1990). Speke Airport was built close to the Hall, starting in 1930 and was officially opened in 1933. The lake is man-made, over 300 years old and located in South Merseyside approximately 11km from Liverpool City Centre. It is close to a number of major industrial sites including chemical, pharmaceutical and manufacturing industries, John Lennon airport and the Ford car production facility. The lake is self contained and surrounded by woodland, with no fluvial input or output at the present time, therefore the majority of contributions to the sediment are from atmospheric sources and the surrounding vegetation. The lake has a surface area of 4050m^2 and a maximum depth of approximately 4m. It is used for fishing by a local angling club and, occasionally, the surface is dragged to remove lilies (Ian Ford, Estate Warden, Speke Hall, pers. comm.).

Figure 7: Speke Hall Lake (Yellow circle shows core sample location).

One sediment core was taken in December 2005 from a boat in the middle of the lake (i.e. deepest part = yellow circle) at Speke Hall using a gravity sediment corer (Boyle, 1995). The water was approximately 4m deep. The core was extruded into

1cm sections in the field and placed into labelled, pre-cleaned glass jars. These jars had been pre-cleaned and ashed for 12 hours at 400°C.

4.2 Initial Sample Preparation and Storage

On return to the laboratory, all cores were frozen (to limit degradation of organic compounds in the sediment), stored in the dark and freeze dried as soon as was practical. Wet storage of sediment is acceptable for short term storage, as long as the samples are frozen and kept in the dark and further processing occurs as soon as is possible (Thomson *et al.*, 1980).

Of the wide variety of methods available for sample preservation, freeze drying is acknowledged to be the one that best preserves the sediment. Unlike oven drying it limits the chances of the formation of aggregates (Loring and Rantala, 1992) and prevents any thermal transformation of the chemical and magnetic properties of the samples. It also limits microbial activity (Bartlett and James, 1980).

Air and oven drying are acceptable methods of sample preservation if total metal concentrations are the only parameters to be analysed but, as the interest was in studying the magnetic parameters and organic pollutant contamination of the sediment, freeze drying was the best method to use. It has been shown that organic matter and $Mn^{(II)}$ solubility and exchangeability increase after air drying, which leads to an increase in the release of Mn and other organic bound trace elements (Bartlett and James, 1980). Freeze drying is not a recommended method of preservation if metal speciation is to be investigated (Hjorth, 2004).

4.3 Inorganic Analysis

4.3.1 Environmental Magnetism

This is the process of using magnetic measurement techniques (such as those developed for palaeomagnetic studies) to describe a variety of environmental processes. One of the main advantages of measuring the magnetic properties of samples is that it is a relatively quick process when compared to traditional

geochemical methods. Another advantage is that the sample is not destroyed by the magnetic analysis and can be reused if more complex geochemistry is required. Susceptibility can also be measured in the field using portable equipment.

The motion of electrons in their orbits governs the magnetic properties of all substances to some degree. This is either the orbital movement round the nucleus of an atom or the spin of the individual atoms on their own axis. In most cases the responses of material to either an applied or measured field are due to the properties of crystals within the material, including their size and shape (Thompson and Oldfield, 1986).

The various parameters are sensitive to chemical and thermal effects, can be used to identify the origin and type of mineral, to investigate the background magnetic field when the sediment was deposited, the rock cooled or the crystals were being formed (Thompson and Oldfield, 1986).

Mineral magnetism can be divided into five categories depending on the behaviour of the mineral in a magnetic field.

1. Diamagnetism

Is an extremely weak property and is often masked by stronger magnetic types. It is recorded as a negative magnetisation and produced by the orbital motion of the electrons and their reaction to an applied magnetic field (Thompson and Oldfield, 1986). In diamagnetic materials (quartz, water, feldspar) the spin motion of the electrons is not a factor in their overall charge as the electrons are all paired and their spin motions cancel out. The magnetisation is also not affected by temperature (Thompson and Oldfield, 1986).

2. Paramagnetism.

This is due to the possession of a permanent magnetic dipole moment by the atoms, ions or molecules. The applied field causes the electrons' spin moments to orientate with the direction of the field. These produce a positive weak magnetisation as the dipoles align themselves parallel with the applied field. Paramagnetism is not a permanent charge as, once the field is removed, thermal agitation breaks down the

alignments. However, a balance is reached between the magnetic ordering and the thermal agitation processes, meaning that the overall charge is relative to the applied charge and the absolute temperature (decreasing as the temperature increases). Paramagnetism is dominant over diamagnetism and common paramagnetic substances are biotite, olivine, carbonates of iron and manganese, the incompletely filled inner electron shells of which are responsible for the spin magnetic moments due to unpaired electrons (Thompson and Oldfield, 1986).

3. Ferromagnetism

In materials with ferromagnetic properties, such as iron, the magnetic properties are highly dependent on temperature. Each material has a Curie temperature above which thermal energy breaks down the magnetic ordering and causes it to behave as a paramagnet. Below the Curie point the material has a strong remanent magnetisation which exists even without the presence of a magnetic field (spontaneous magnetisation). This is due to exchange interactions caused by the parallel alignment of all the elementary magnetic moments of neighbouring electrons due to the effects of quantum mechanics (Thompson and Oldfield, 1986). The strength of these effects allows the alignment of the magnetic moments even with the disturbance caused by thermal effects.

4. Antiferromagnetism

In this type of magnetism all the magnetic particles have the same charge but they are in opposite directions in neighbouring atoms. This leads to an overall zero magnetic charge on the material. If the opposing charges are not perfectly aligned then there will be a weak overall magnetism (known as spin canting) (Thompson and Oldfield, 1986).

5. Ferrimagnetism

This is similar to antiferromagnetism with opposing charges acting in opposite directions. However, unlike antiferromagnetim there is a strong overall charge as the magnetism in one direction is higher than in the other.

There are a variety of methods used in the laboratory to measure magnetic properties of substances these include:

Isothermal Remanent Magnetisation (IRM).

This is the magnetisation that is acquired by a sample after being exposed to a magnetic field at a given temperature (usually room temperature). The level of remanance acquired is dependent on the field applied to the sample and can, therefore, be altered by placing the sample in fields of increasing strength (Thompson and Oldfield, 1986). Samples are exposed to the field then removed and measured to obtain the 'remanance' value. This is proportional to the abundance of ferromagnetic minerals present in a given grain size and mineralogy (Thompson and Oldfield, 1986) and decreases with increasing grain size. The highest Isothermal Remanance that can be produced in a sample is called the Saturation Isothermal Remanance Magnetisation (SIRM) and is related to the magnetic grain size (higher in small single domain grains - less than 0.1 μm, than in larger multi-domain grains). A laboratory induced SIRM may not be the actual SIRM as the equipment being used may not be capable of producing this on certain samples e.g. those high in haematite (Thompson and Oldfield, 1986).

Anhysteric Remanent Magnetisation (free from hysteresis) (ARM)

Is generated in a sample by the application of a strong alternating field which is gradually reduced to zero in the presence of a small direct current field. It is related to magnetic grain size (Thompson and Oldfield, 1986).

4.3.1.1 Magnetic Parameters

This study uses the following magnetic parameters to investigate the samples being analysed. These are all implemented at room temperature due to the chemical changes that can be caused to the samples by using high temperate studies.

Susceptibility (χ) is a method of measuring how easy it is to magnetise a sample – it is measured in small fields (usually less than 1mT) and, at this field strength, is found to be independent of the strength of the applied field and is related to magnetite concentration. When magnetite is present in small amounts then χ is weak and can be influence by diamagnetic and paramagnetic substances (Thompson and Oldfield, 1986). It is proportional to the amount of ferrimagnetic minerals present (iron oxides)

as well as paramagnetic minerals such as iron bearing silicates (Georgeaurd *et al.*, 1997). Susceptibility is reduced by the presence of diamagnetic substances. It is a very useful technique to use as an initial indicator of the magnetic potential of a site. χ is measured using two frequencies to obtain low frequency (χlf) and high frequency (χhf) values. It has also been shown to be related to magnetic grain size (Maher, 1988[b]).

SIRM gives an approximate concentration of the total remanance carrying minerals in a sample and can be affected by magnetic grain size (Maher, 1988[b]).

The FD% is the difference between low field and high field susceptibility (χlf-χhf) expressed as a percentage of χlf. It is useful in detecting the presences of viscous ferrimagnetic grains with stable single domain / superparamagnetic (SP) boundaries (Oldfield, 1991). It is dependent on very small grained particles (fines) so can be used to indicate the grain sizes present. If it is lower than 2, it indicates that there are virtually no SP grains; 2-10 indicates a mixture of SP, SSD (Stable Single Domain) and MD (MultiDomain) grains; 10-14 indicates that the sample contains virtually all SP grains and results over 14 indicate an error or contamination with metal (Muxworthy, 2001).

Susceptibility of ARM (χARM) is influenced by the concentration of magnetic minerals but can also indicate the presence of fine grained SSD magnetites (around 0.03-0.05um diameter. SSD possess high values of χARM (Maher, 1988).

Soft (Low field Isothermal Remanance) shows percentage of magnetite (remanance bearing ferrimagnets) type grains (Dearing *et al.*, 1997).

Hard (High field Isothermal Remanance) shows percentage of Haematite and Goethite in a sample (Yang, 1997).

χARM/SIRM has been used as a proxy for grain size (Thompson and Oldfield, 1986; Maher, 1988) and an increase in this ratio can suggest a decrease in grain size if the dominant mineral is magnetite. χARM/SIRM is an indicator of the mean magnetic grain size with higher values indicating more SSD grains (Yang, 1997).

SIRM/χlf varies inversely with magnetic grain size or, in the case of a low ratio it indicates the presence of paramagnetic minerals (Maher, 1988).

χARM/χlf varies inversely with magnetic grain size.

HIRM (Hard IRM) is related to the proportion of haematite and goethite in the sample (Dearing *et al.*, 1997).

Increases in χlf, χARM and SIRM can indicate higher levels of concentration of magnetic minerals (it should be noted that these parameters are also grain size dependent). High concentrations of non-SP coarse minerals can be due to the underlying geological deposits weathering (Hay *et al.*, 1997).

High values of χlf and %FD indicate presence of SP grains (Foster *et al.*, 1994; Dearing *et al.*, 1996). A decline in χlf and χARM indicate declining ferromagnetic grains. The ratio of χlf to HIRM might be low if goethite and lepidocrocite are precipitated in preference to magnetite (Dearing *et al.*, 2001).

Higher SIRM, χARM and Soft values indicate more magnetite in samples. Higher Hard indicates more imperfect antiferromagnetic minerals such as goethite and Haematite. Oldfield (1994) and Van der Post *et al.* (1997) have shown that SSD and SP magnetic particles are concentrated in the clay particle size range (therefore high values of indicators of these would indicate high concentration of clay particles in the sediment) (Oldfield and Wu, 2000).

4.3.1.2 Magnetic analysis

Samples for analysis of environmental magnetism were wrapped in cling film and placed in 10ml plastic pots (Alzon BGG440P Specimen jar, Barloworld Scientific Ltd). The pots and cling film had been preweighed and each was reweighed once the sediment sample had been packed inside.

Low frequency and high frequency susceptibility (0.4 kHz and 4.7 kHz respectively) measurements were made on each core sample using a dual frequency Bartington Magnetic Susceptibility Meter. The Bartington Magnetic Susceptibility Meter was calibrated before each set of samples were analysed.

Anhysteric remanent magnetisation was generated using a Molspin AF demagnetizer and measured using a minispin slow speed spinner Fluxgate magnetometer.

Isothermal remanent magnetisation and related parameters were generated using a Molspin Pulse Magnetiser and measured using the fluxgate magnetometer. Fields measured were 1T (SIRM) and reverse fields –20mT and –300mT.

4.3.2 Metal Analysis

4.3.2.1 X-Ray Fluorescence

Sediment samples were analysed using X-Ray Fluorescence (XRF) to identify the elements present in each sample. XRF has been used by many workers (Plater *et al.*, 1998; Boyle, 2000, Grayson and Plater, 2008) for metal analysis as it is a relatively cheap and easy method of obtaining data on the elements present. Rathburn *et al.* (1996) showed that XRF gave good correlation with metal analysis done by atomic absorption spectrometry.

The Oglet Bay sediments were analysed using an isotope source system. Disaggregated sediment (~0.5g) was packed into polythene containers with a tightly fitting sleeve and a Polypropylene film was stretched across the base of the container. The Speke Hall, sediments were packed into plastic holders (as above) and then analysed by a Braker Axis S2 Ranger XRF and the data processed to account for LOI using the software Spectra EDX.

There are problems associated with the use of XRF for metal analysis, as it is not sensitive enough to detect low levels of certain metals (Cd, Se), light elements such as Li cannot be analysed and neither can volatiles such as Hg (Ridgeway and Shimmield, 2002).

For both machines, standard reference materials were used to check the accuracy of the XRF (Buffalo River Sediment, San Joaquin Sediment, Pond Sediment and Stream Sediment).

4.3.2.2 Flame Atomic Absorption Spectrometry (FAAS)

As they could not be detected using XRF, Cadmium and Mercury were analysed by FAAS, (Thermo Electron Corporation S Series AA Spectrometer). This is a common technique for identification of both these metals (Boyle, 2001).

Cd analysis.

Cadmium levels were recorded using an air/acetylene flame with a Slotted Tube Atom Trap and autosampler giving accuracy to 0.004mg/L.

Hg analysis

Mercury concentration was assessed using an air/acetylene flame and a cold vapour sample injection method.

Sample Preparation

A nitric acid digest was used to extract the metal for analysis.

0.25g of sediment and standards were accurately weighed into acid washed centrifuge tube. Concentrated nitric acid (2mL) was added to each centrifuge tube. The tubes were placed in a water bath at 90°C for 1 hour, then removed and allowed to cool. Double distilled water (12mL) was added to each centrifuge tube and the tubes placed on a flat bed shaker overnight. The following day, the settled sediment was resuspended in the tubes which were then centrifuged at 1200rpm for 20 minutes. The supernatant was decanted off into AA tubes and placed in the fridge until needed for analysis.

4.3.4 Particle Size Analysis

Many metals and organic pollutants preferentially adsorb to the finer grained sediments (Olsen *et al.,* 1982). Grain size analysis was carried out to try to eliminate the chance that any high pollutant concentrations recorded were due to high concentrations on fine grained sediment particles rather than a pollution input. Particle size analysis was done to identify the range of grain sizes present in the samples so that correlations could be undertaken to identify which (if any) parameters had apparent grain size controls on their behaviour.

Grain Size phi	Grain Size mm/μm	Descriptive Terminology	
-11	2048mm	Very large	Boulders
-10	1024	Large	
-9	512	Medium	
-8	256	Small	
-7	128	Very small	
-6	64	Very coarse	Gravel
-5	32	Coarse	
-4	16	Medium	
-3	8	Fine	
-2	4	Very fine	
-1	2	Very Coarse	Sand
0	1	Coarse	
1	500μm	Medium	
2	250	Fine	
3	125	Very fine	
4	63	Very coarse	Silt
5	31	Coarse	
6	16	Medium	
7	8	Fine	
8	4	Very fine	
9	2	Clay	

Table 1: Particle Size Class Definitions (taken from Blott and Pye, 2001).

Analysis was carried out using a Coulter Laser Granulometer. A small amount of each sample was placed on a watch glass with Calgon to disaggregate it and then washed through the machine. The results were computed using the computer program 'Gradistat' (Blott and Pye, 2001) and presented using the Folk and Ward (1957) method and particle size classification (Table 1) was taken from Blott and Pye (2001).

Results were presented as particle size distribution, mean grain size, skewness (the preferential spread of distribution to one side of the average), kurtosis (the degree of grain concentration relative to the average), the amount of sorting and the percentage of sand and mud in the sample (Blott and Pye, 2001). The '% Sand' grain size fraction refers to grain sizes above 63μm whilst the '% Mud' fraction is particles under 63 μm.

4.4. Organic Geochemistry

4.4.1 PCB and PAH Sediment Extraction Methodology

PCBs and PAHs adsorb strongly to sediment and so to analyse their environmental concentrations they need to be released from the sediment for quantification by gas chromatography. In this study an ultrasonic method was used to extract PCBs and PAHs from the sediment samples for analysis by Gas Chromatography - Electron Capture Detection (GC-ECD) and Gas Chromatography- Mass Spectrometry (GS-MS) respectively. Ultrasonic extraction has been shown by many authors to be a good method of extracting PCBs and PAHs from soils and sediment. It has the advantage over Soxhlet extraction of being quicker and cheaper, using fewer solvents, (Aydin, 2007) and giving recovery rates of between 60% and 80% (Song *et al.,* 2002; Banjeroo 2005[a] and 2005[b]; Ratola *et al.,* 2006; Barco-Bonilla *et al.,* 2009).

Samples (~5g) were weighed into clean centrifuge tubes and internal standards (deuterated D10 anthracene and octochloronaphthalene) were added and the sample covered with a 1:1 hexane:acetone solvent mix. The centrifuge tubes were placed in an ultrasonic bath (Sonicor Instrument Corporation) for 30 minutes, removed and centrifuged using a Jouan MR23*I* centrifuge, at 2500 rpm for 5 minutes at 18°C. The supernatant was then pipetted into a pear shaped flask containing spongy copper (to remove any elemental sulphur) and the centrifuge tube was topped up with solvent again to repeat the extraction process (x3 total). Once this was complete, the solvent was evaporated off under nitrogen, the flasks sealed with PTFE tape and left in the freezer overnight to allow as much of the sulphur as possible to react with the spongy copper. The following day, each sample was redissolved in hexane:acetone (1:1) and rinsed through a pipette packed with extracted cotton wool to remove the spongy

copper. The solvent was evaporated off under nitrogen and the sample redissolved in a small amount of solvent and rinsed through an alumina packed glass column.

Sulphur has to be removed because it interferes with mass spectrometry by giving erroneous results with molecular weight distribution (Blumer, 1957) and the alumina and silicalite columns are used to remove n-alkanes which can interfere with PCB analysis. It should be noted that lower branched n-alkanes (< C16) can pass through the silicalite clean up (Thompson *et al.,* 1998), however, enough of higher molecular weight ones are removed to leave the samples clean enough to give good results with GC-ECD.

The alumina was heated to 800°C for 4 hours and left overnight at 200°C, allowed to cool and deactivated (5%) by adding milli-Q water to it and shaking it for 30 minutes. 9.5g of alumina was 5% deactivated by mixing with 0.5g of MilliQ water. The first 2mL of the sample was eluted through the alumina column using pesticide grade hexane and collected for PCB analysis and the next 10mL rinsed through using dichloromethane:hexane (1:1) and collected for PAH analysis. The solvent was evaporated under nitrogen and they were stored in small vials with activated copper turnings (to remove any remaining sulphur) in the freezer prior to analysis.

The samples for PCB analyses underwent further clean up using silicalite. A clean pipette was packed with extracted cotton wool and filled with silicalite that had been heated to 550°C for 4 hours and left overnight at 200°C,

This method has been used successfully in the past to clean up samples that are from areas with high levels of pollution, particularly hydrocarbons (Thompson *et al.*, 1998). The n-alkanes sorb to the silicalite whilst the PCBs are not retained. Thompson *et al.* (1998) have shown that very few (if any) of the PCBs present in a sample are trapped on the silicalite column.

4.4.2 PCB and PAH Concentration Analysis

Samples were then analysed for PCB content using GC-ECD and PAHs using GC-MS. Samples were analysed in random order to avoid systematic errors.

The PCB congeners that were determined were: The trichlorobiphenyls 18, 28; the tetrachlorobiphenyls 44, 47, 49, 52, 66; the pentachlorobiphenyls 101, 105 118; the hexachlorobiphenyls 128, 138, 141, 151, 153, 156, the heptachlorobiphenyls 170, 183, 180 and the octochlorobiphenyl 194. The PCBs were identified using retention times. It should be noted that the assumption was made that each peak in the chromatograph was produced by a single congener and those co-eluting could not be separated, so it is possible that concentrations of these have been overestimated. For example, PCB 66 co-elutes with 95, 138 co-elutes with 160 and 170 co-elutes 190.

The following PAHs were determined: acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, dibenz[a,h]anthracene. These PAHs were chosen because they are amongst the most toxic, have the highest concentrations in the environment and are those to which the population is more likely to be exposed.

Commercially available PCB standards and PAH standards were run at intervals to assess relative retention times of PCBs and PAHs. Each of these standards was chosen to include all the PCBs and PAHs mentioned above and to cover some of the more toxic congeners.

4.4.2.1 GC-MS

GC-MS analyses were performed using a Trace GC fitted with an on-column injector. The gas chromatography oven temperature was programmed as follows: 50 °C isothermal for 1 min, 5° C/min to 300 °C; isothermal at 300 °C for 5min; 10°C/min to 315 °C, and 5min at 315 °C. The sample was directly injected onto a fused silica capillary column (25m, 0.2mm id., 0.25μm film thickness, BPX-5) with a deactivated retention gap which was introduced directly into the chemical ionisation source of a Thermo-Quest TSQ-7000 mass spectrometer. Helium was used a carrier gas and methane (source pressure ca 5600mT) (for the PCB determination) as reagent gas for negative ion chemical ionization (NICI). Typical operating conditions were: electron voltage, 200eV; emission current, 300μA, multiplier, 1240V; source temperature 170 °C. The syringe was rinsed 30 times with hexane between injections to limit cross-contamination between samples and standards.

PAHs were identified from their full scan spectra when possible, and by comparison of their relative retention times with those of the authentic standards. Five standard mixtures (between 0.25 and 5ng/μl) of individual PAHs were used for calibration purposes and for the determination of relative response factors. A daily three-point calibration was used to compensate for minor variations in source conditions. Canadian marine sediment HS-2 was used for quality control. A full procedural blank extract was also analysed. Xcalibur software (Version 1.0) was used to acquire and process the data. GC-MS is a standard method that has been used by many authors for identifying PAHs in sediment (Davies and Wolff, 1990; Liu, 1999; Liu, *et al.,* 2000; Gocht *et al.,* 2001; Yang *et al.*, 2008).

To test reproducibility a number of samples were run in triplicate and used to estimate the variability of the samples.

4.4.2.2 GC-ECD

GC-ECD analysis was performed using an Agilent 6890N GC with an electron capture detector. The gas chromatography oven temperature was programmed as follows: 50°C isothermal for 1 min, 8°C/min to 200 °C; isothermal at 200°C for 4min; 10°C/min to 315°C, and 15min at 315°C. The GC was fitted with a fused silica capillary column (25m, 0.2mm id., 0.25μm film thickness, BPX-5) and 1μL of sample was injected *via* a heated injector (320°C) in splitless mode. Helium was used a carrier gas.

PCBs were identified by comparison of their relative retention times with those of the authentic standards. Five standard mixtures (between 0.0125 and 0.2ng/μl) of individual PCBs were used for calibration purposes and for the determination of relative response factors. A daily calibration was used to compensate for minor variations in source conditions. Canadian marine sediment HS-2 was used for quality control. A full procedural blank extract was also analysed. Chemstations software was used to acquire and process the data.

4.5 Pre- and Post-Extraction Metal Comparison

A comparison was run between Speke Hall samples that had been extracted for PCB and PAH analysis and those that hadn't been extracted. This was done to investigate differences in sediment metal concentrations between samples that had been subjected to an organic solvent extraction and those that hadn't. Subsamples of extracted and non-extracted 1cm core section were analysed by XRF and FAAS in the same way as for the other samples. The data were analysed using a paired sample T-test and a Wilcoxon Matched Pair test to determine any significant difference between the metal levels in each group.

4.6 Organic Matter Analysis

4.6.1 Loss on Ignition (LOI)

Loss on ignition (a common method to measure organic content of samples without removing structural water from inorganic components) was also recorded for the samples (Ball, 1964). Approximately 0.5g of freeze dried sediment was placed into preweighed glass beakers and oven dried overnight at 105°C. The beakers where then cooled and reweighed before being heated to 450°C for 4 hours and then reweighed. Loss On Ignition was calculated for each sample using a preformatted spreadsheet calculation.

4.6.2 Total Organic Carbon and Nitrogen.

The sediment samples were analysed for Total Organic Carbon (TOC) and Nitrogen concentrations using a Carbo Erba NC 2500 CHN Elemental Analyser. Samples were analysed in triplicate with a reproducibility of $\leq \pm 10\%$. Following de-carbonation TOC was determined by the acid vapour method developed by Yamamuro and Kayanne (1995).

4.7 Wind Data

Wind data were obtained from the British Atmospheric Data Centre (BADC). It was processed using the software WINDROSE PRO, Version 2.3.11 (Enviroware.com) which allowed the creation of Wind Roses showing mean wind direction and mean

wind speed for each of two locations. The mean hourly prevailing wind speeds and direction were plotting for a site at Speke and a site near Manchester airport. The Speke data encompasses the period 1969 to 1998, whilst the Manchester data was for 1949 to 1995.

4.8 Statistical Analysis

Statistical analysis was carried out using the program SPSS 16 and Primer-E 6

4.8.1 Matched Pair T-test and Wilcoxon Test

The experiment to test whether the extraction process for PCB and PAHs made a significance difference to the metal levels detected in the sediment by XRF and AA was tested using a Matched Pair Student's T-Test and a Wilcoxon test. Both these tests measure whether or not there is any difference between 2 sets of data (in this case the extracted and unextracted sediment) and whether any measured difference is significant.

4.8.2 Correlation Coefficients

Pearson Product Moment Correlation coefficients were run for the metal, PCB, PAH, Magnetics and Grain size data to investigate whether there was a relationship between any of the parameters. For example, did a change in one parameter relate to a change in another parameter and, if there was a relationship shown, was it a significant relationship or did it occur by chance.

It should be remembered that a 'significant' correlation is not necessarily proof of a causative relationship between the data (Lewis and Trail, 1999) and to allow for this correlations were taken to be strongly significant if they were over 0.7, i.e. 49% or more of the variance could be explained by the correlation rather than by coincidence. However, weaker correlations (under 0.7) that have been highlighted by SPSS as showing a significant relationship within the data have also been discussed. SPSS gives the correlations at both the 0.01 and 0.05 levels of significance. Those parameters that showed a relationship at the 0.01 level could be considered as strongly significant, as a chance relationship between the data would only occur 1% of the time, whilst those at the 0.05 level were less significant, as a chance

relationship could occur in these cases 5% of the time. Both strong (above 0.7) and weak (below 0.7) negative and positive correlations have been considered in the results, as even weak correlations suggest a relationship between the data which could have been reduced by the complexity of interaction in the environment.

A positive correlation is one where as one set of data being compared increases so does the other one and a negative correlation occurs when the values in one data set decrease as the values of the comparison set increase (Lewis and Trail, 1999).

4.8.3 Principal Component Analysis

In an attempt to identify which of the parameters analysed were of the greatest importance, Principal Component Analysis (PCA) was undertaken using the computer programme 'Primer-E6'. Data was normalised using the function in the program and then to correct for skewed data either a square root or fourth root correction was applied followed by PCA. The data was analysed using a scatter plot Eigenvalues and Eigenvectors.

4.8.4 Statistical Analysis of the Health Data

The methods used to plot Hotspot clustering of the health data and to compare the health data with the historical pollution data are discussed in Appendix Two.

4.9 Pollutant/Element Concentration Guidelines

As a method of assessing whether or not an element was present in unnaturally high concentrations, Average Shale Values (ASV) (Turekian and Wedepohl, 1961) were used (Table 2).

Average Shale Values (ASV) were used to give an indication of which metals where present in enriched amounts. In general ASV give an idea of the natural background concentrations of elements that should be found in sediments, i.e. those that come from geological sources. Average Shale is a convenient method of identifying 'above background' levels of metal that could be due to pollution input. It has been used by a number of authors (Forstner 1993, Grousset *et al.*, 1995; Turner 2000) as part of studies investigating metal concentrations in the environment. It was used in this

study because it more closely matches the background metal concentrations found in the more fine grained sediment present in the Mersey estuary, whereas another measure of metal concentrations 'Upper Crustal Values' (Turekian and Wedepohl, 1961; Taylor and McClennan, 1995) gives better results for a wider range of grain sizes. In an ideal situation, the best method would be to get background levels from uncontaminated catchment samples (soils and river sediments) drawn from a wider area in the region or take a core deep enough to sample from a pre-pollution era. There are other methods of assessing metal contamination levels in a location. Some authors (Hutchinson and Rothwell, 2008) use Sediment Quality Guidelines (CCME 2002), Soil Guideline Values (DEFRA 2002) Soil Intervention Levels (NEPC 1999) or even Pollution Load Index (Tomlinson *et al.*, 1980; Harikumar *et al.*, 2009). Sediment Quality Guidelines and Soil Guideline Values for selected metals have been used in Chapter 11 of this study to assess pollution between the cores.

Average Shale Values for the metals analysed					
SI mg/g	Ti mg/g	Ca mg/g	K mg/g	Fe mg/g	Mn mg/g
273	4.6	22.1	26.6	47.2	0.85
S mg/g	Cl mg/g	Pb µg/g	Zn µg/g	Br µg/g	Zr µg/g
2.4	0.18	20	95	4	160
Rb µg/g	Sr µg/g	Cr µg/g	Ni µg/g	Cd µg/g	Hg µg/g
140	300	90	68	0.3	0.4
Al mg/g	P µg/g	As µg/g	Ba µg/g	V µg/g	CU µg/g
80	700	13	580	130	45

Table 2: Average Shale Values.

However, as ASV are an 'average' value, they do not take into consideration any variation caused by local geology. This can be seen from the results that show certain elements as having concentrations lower than the ASV, e.g. Si, Ti and K, with Fe being significantly under these values. It is likely that the reason these are so low is due to the influence of the regional geology. On the other hand, those elements that are found in significantly higher concentrations than the ASV (Pb and Zn), are often (but not always) likely to be present due to the influence of man and pollution inputs. Chlorine and Br levels are also significantly higher than the Average Shale Values and this could be due to the influence of Cl and Br ions from seawater or possibly due to pollution from the chloride industry on the Mersey. Sr can be released from Zn refining which could explain the weak positive correlation with Zn

4.10 Disease Incidence Data

Disease Incidence data for the region is included in Appendix 2. Disease Incidence is the number of new cases diagnosed in a defined population over a defined period of time. Disease data were obtained in a number of varying formats as outlined below.

SMR: Standardised Mortality Ratio

SMR is a method of calculating whether or not mortality from a disease is above or below what would be expected in an area. It is calculated by dividing the number of observed deaths from a disease by the number expected in the area and multiplying the answer by 100.

SAR: Standardised Admission Ratio

SAR is a similar ratio obtained by dividing the number of actual hospital admissions for a disease by the number expected for the area.

DSR: (Directly Age Standardised Rates)

DSR is calculated by taking the age specific rates and applying them to the age distribution of a hypothetical population, in this case the 'Standard European Population' and expressed as a rate per 100,000 people.

Age Standardisation of data is a method used to allow comparisons between populations with different age distributions, either in different areas or in one area over a period of time. They are calculated from a weighted average of age specific rates, (for example, the age specific rate for each 5 year age group) and then compared with the European Standard Population. Crude rates are obtained by dividing the number of cases or deaths by the population at risk.

4.10.1 Renal Disease and Heart Disease Data

Renal disease data and heart disease data were provided by Dr Alex Stewart from the Health Protection Agency and were obtained from hospital admissions, diagnosis data and mortality data. The data was provided as census area Lower Super Output Area data and included actual disease occurrence data and Standardised Mortality Ratio (SMR) data (for Renal Disease) and actual occurrence and Standardised

Admission Ratio (SAR) data for heart disease. Renal disease data for Warrington, (2003-2005, all ages, renal disease not secondary to other causes) includes: acute nephritic syndrome; rapidly progressive nephritic syndrome; recurrent and persistent haematuria; chronic nephritic syndrome; nephrotic syndrome; unspecific nephritic syndrome; isolated proteinuria with specified morphological lesion; acute tubulo interstitial nephritis; other chronic tubulo interstitial nephritis; chronic tubulo interstital nephritis, unspecified; other specified renal tubulo interstitial diseases; chronic renal failure; unspecified renal failure; unspecified contracted kidney; malignant neoplasm of kidney,

The Heart Disease data for Liverpool, (2003-2005, under 75 year olds) includes the following causes: angina pectoris; acute myocardial infarction; subsequent myocardial infarction; current complications after MI; other acute ischaemic heart disease; chronic ischaemic heart disease.

Using the computer programme ArcView, this data was plotted on a map of the region to show local distribution.

4.10.2 Cancer Data

The cancer data was obtained from the National Cancer Intelligence Network from their online publication National Cancer E-Atlas:
http://www.ncin.org.uk/index_files/eatlas.htm

The data are a record of each new cancer case diagnosed. It does not contain secondary cancers and reoccurrences and are reported for the calendar year it was diagnosed in using Direct Age Standardised Rates.

CHAPTER 5
OGLET BAY UPPER MARSH CORE RESULTS

The following chapter is a description of the results from the sediment core taken from the upper marsh location on the Oglet Bay saltmarsh. It shows the downcore profiles of particle size, magnetic properties, metal concentration, PCB and PAH distribution and also provides a description of the statistical analysis carried out on the data (i.e. correlation coefficients and Principal Component Analysis).

5.1 Upper Marsh Core Particle Size Analysis

Particle size data indicated the sediment varied between a bimodal and a polymodal distribution: it was poorly sorted and dominated by very coarse silt and coarse silt. Using the Folk and Ward (1957) description it was poorly sorted (but showing a progressively better sorting downcore), symmetrical in the top part of the core and fine skewed towards the bottom, and mesokurtic (Figure 9 a-d). Mean grain size shows an overall decrease downcore. The majority of the sediment is mud, but with a sand content of around 20% (Figure 8). The relative percentage of sand decreases towards the bottom of the core, whilst the percentage of mud increases (Figure 9e).

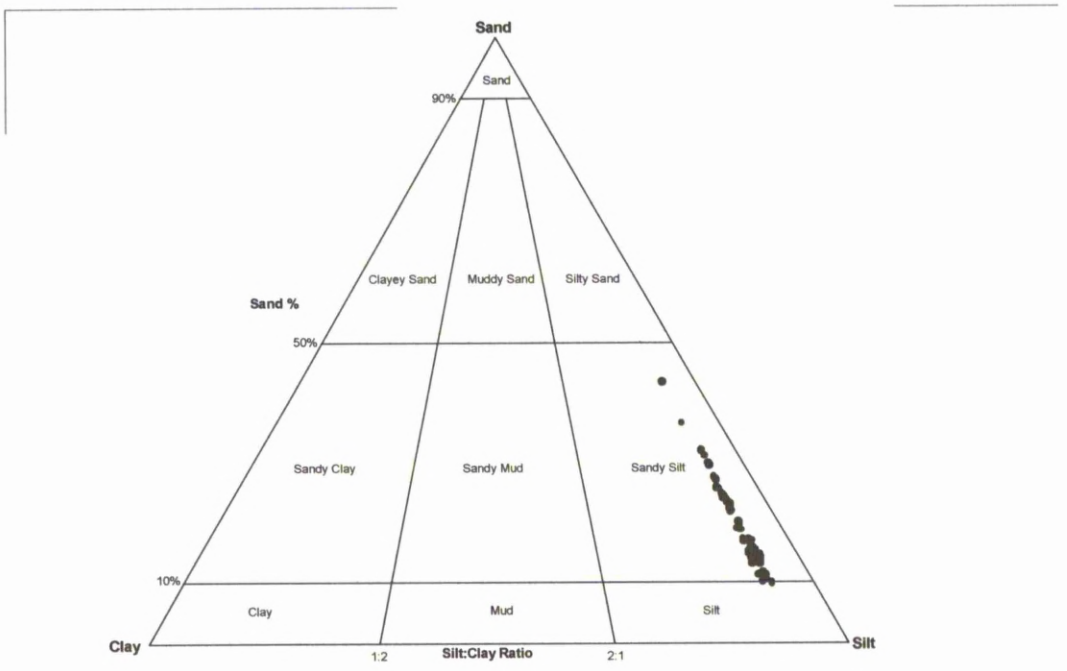


Figure 8: Upper Marsh Core Particle Size Distribution.

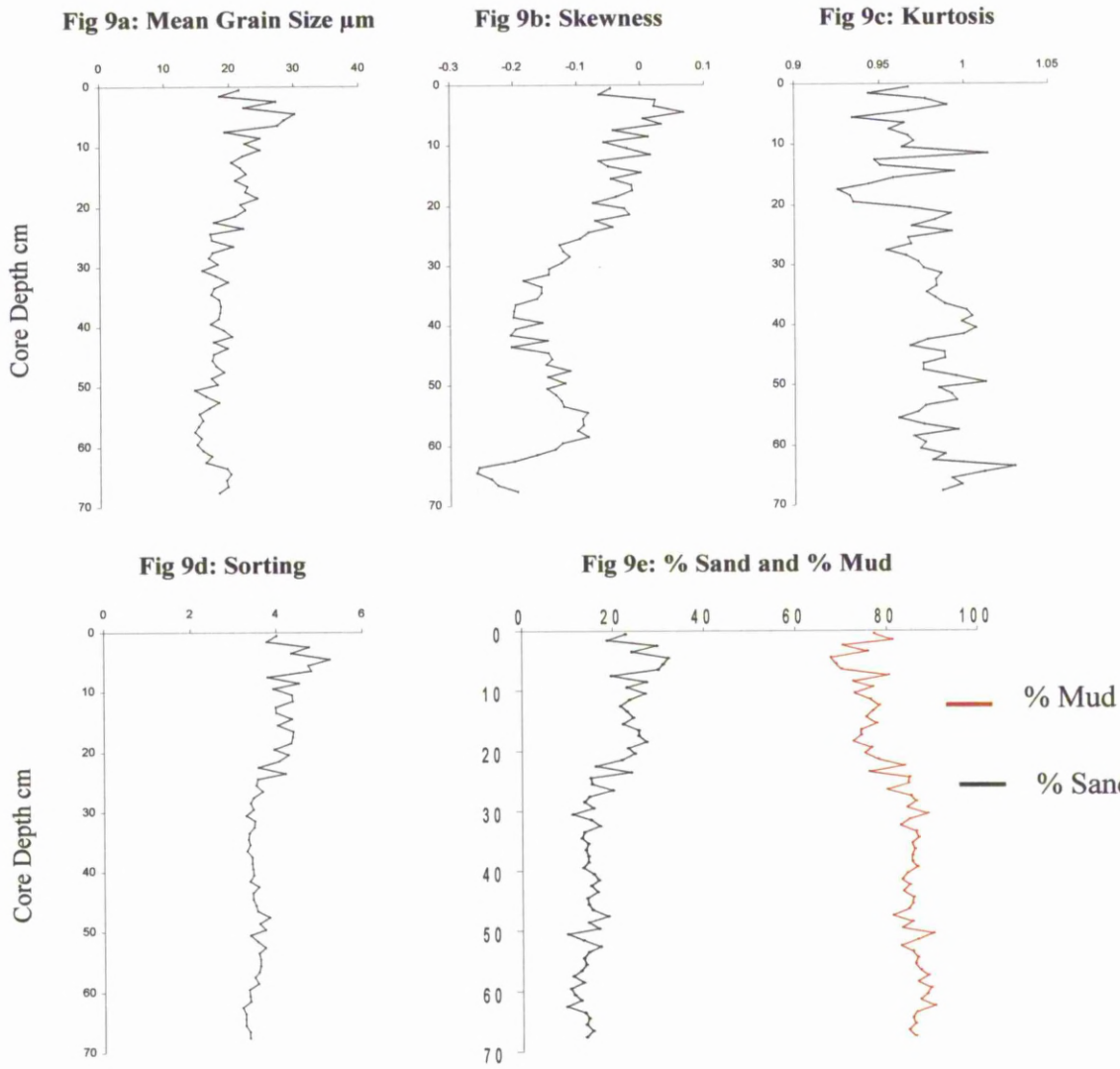


Figure 9a-e: Upper Marsh Core Particle Size.

5.2 Upper Marsh Core Element Data

Al (Fig 10b), K (Fig 10e), Ti (Fig 7c) and Rb (Fig 10j) show fairly steady downcore trends with a relatively small degree of fluctuation and both are below ASV.

Ca (Fig 10d) values show a decrease in the top part of the core (to 9cm) followed by a trend to increase with depth. This is similar to the trend exhibited by Si (Fig 10a), particularly below about 40 cm depth. Although the trend is similar, Si is below ASV whilst Ca is below ASV in the top part of the core but increases in concentration to above ASV from 10cm.

S (Fig 10f), concentrations show an overall increase with depth to 52cm with two large peaks between 24 and 30 cm and 49 and 52 cm. After 52 cm there is a decrease in concentration with depth. Apart from in the top 2cm concentrations are above ASV.

Fe (Fig 10g) shows an increase in the top part of the core (down to 11cm) and then a slight decrease to about 21cm depth followed by a slight increase. It then remains fairly consistent until concentrations start to increase again at around 45cm. Concentrations are below ASV.

Mn (Fig 10h) values are fairly consistent with depth except for a large peak between 4 and 10cm depth which is likely to be the location of a strong redox front. Aside from this peak, concentrations fluctuate slightly either side of ASV.

Cl (Fig 10i) concentrations show a trend to increase in the top 10 cm but then fluctuate considerably to a depth of 60cm, after which they start to decrease. Concentrations are well above ASV.

Zr (Fig 10k) concentrations are above ASV and show an initial decrease in the top 2 cm they then increase slightly to 35cm (except for a large peak at 28cm). They then show a gradual decrease to 50cm where values star to increase towards the bottom of the core.

Cr (Fig 10l), Ni (Fig 10p) and Y (Fig 10t) concentrations fluctuate (both above and below ASV) wildly downcore.

Br (Fig 10m) values show an increase from the top of the core to 6cm where there is then a gradual decrease in concentration which is similar to the trend for Mn. Values are well above ASV.

Cd (Fig 10n) shows an overall downcore increase in concentration and are above ASV. It has major peaks at 22cm and 30cm and a large step-wise increase in

concentration at 45cm. Below this depth concentrations remain fairly stable except for a peak at 63cm.

Hg (Fig 10o) shows a downcore increase in concentration, with a large peak at 57cm, and is well above ASV.

Both Pb (Fig 10r) and Zn (Fig 10q) show an increase with depth to 60cm when there appears to be a slight drop in concentration. There is also a zone of higher concentrations at about 30-36 cm. They are well above ASV.

Sr (Fig 10s) concentrations show a decrease to 6cm followed by an increase to 16cm, after which they decrease to 20cm and then remain fairly constant downcore. They are below ASV.

Loss On Ignition (LOI) (Fig 10u) fluctuates in the top 10cm then values remain fairly consistent down to 48cm (except for a peak at 21cm) after which they show a trend to decrease. This also shows a similarity to the trend of Cl which could indicate that Cl is being controlled by the organic content of the sediment.

Of the metals analysed Cd, Zn, Pb, Hg, Br, S, Cl, Zr are all above ASV whilst Cr, Ni and, to a lesser extent, Y fluctuate above and below ASV. Ca is above ASV in the bottom part of the core and Mn is above ASV in the top part of the core.

Fig 10a: Si mg/g

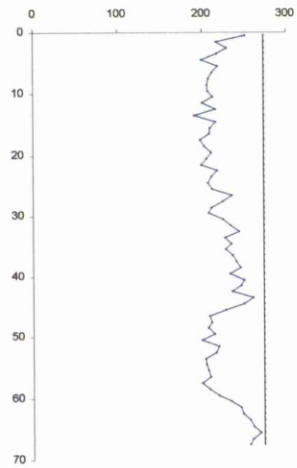


Fig 10b: Al mg/g

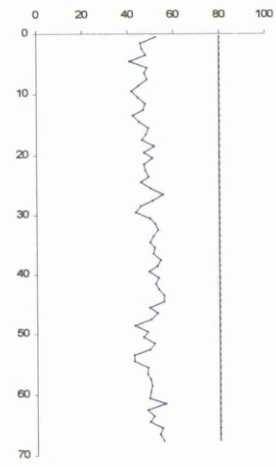
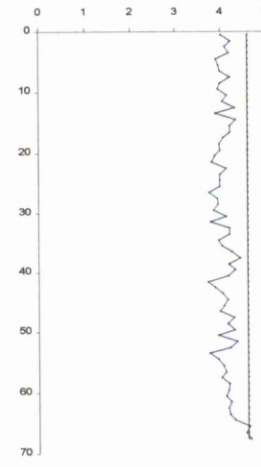


Fig 10c: Ti mg/g



Core Depth cm

Fig 10d: Ca mg/g

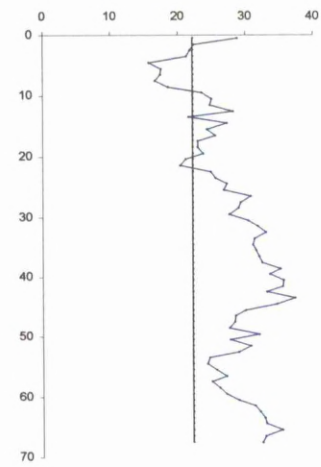


Fig 10e: K mg/g

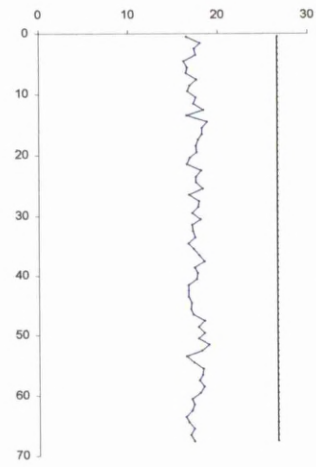
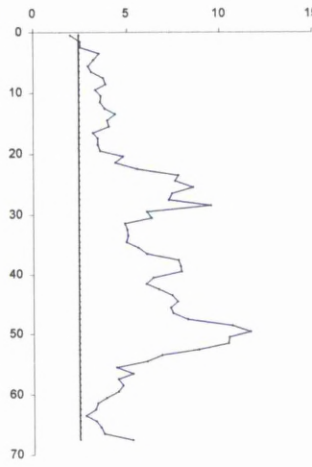


Fig 10f: S mg/g



Core Depth cm

Fig 10g: Fe mg/g

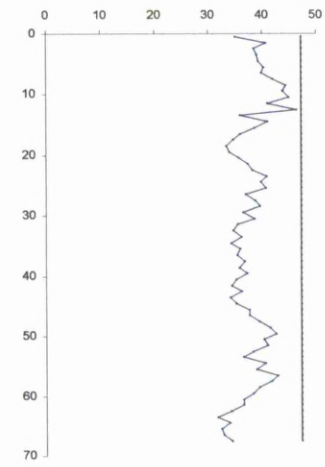


Fig 10h: Mn mg/g

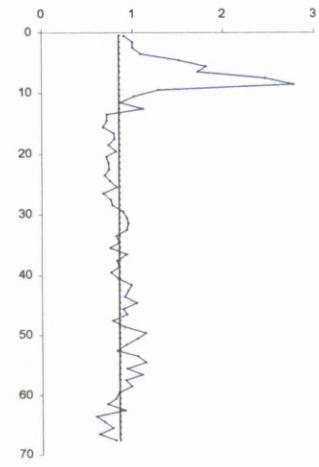
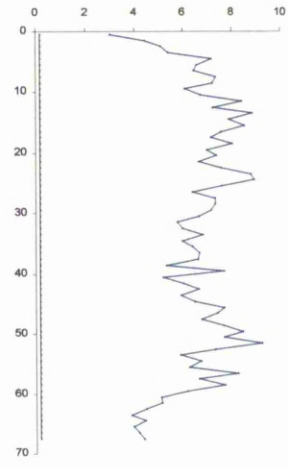


Fig 10i: Cl mg/g



Core Depth cm

Fig 10j: Rb µg/g

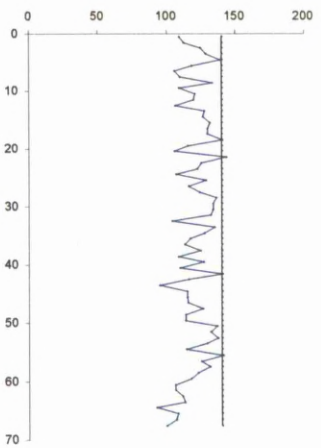


Fig 10k: Zr µg/g

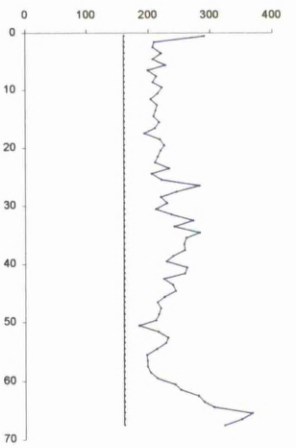


Fig 10l: Cr µg/g

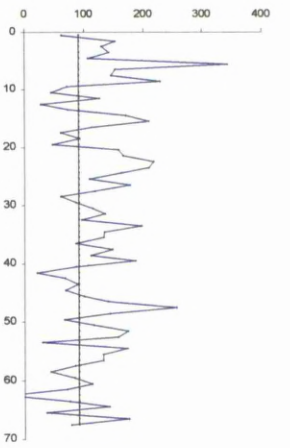


Fig 10m: Br µg/g

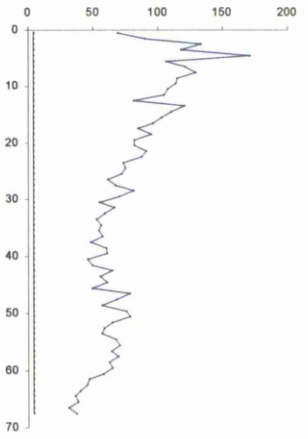


Fig 10p: Ni µg/g

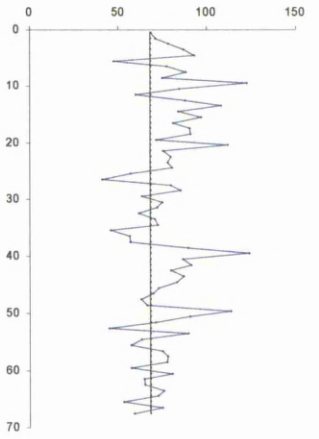


Fig 10n: Cd µg/g

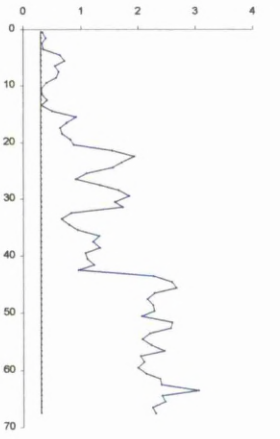


Fig 19o: Hg µg/g

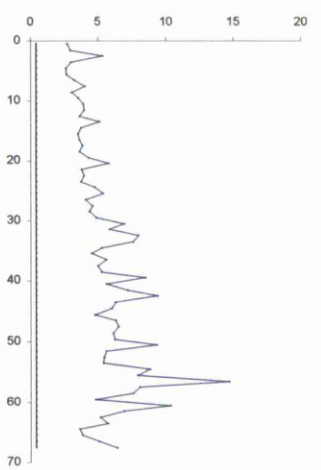


Fig 10q: Zn µg/g

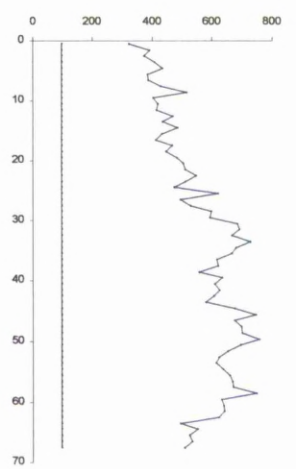
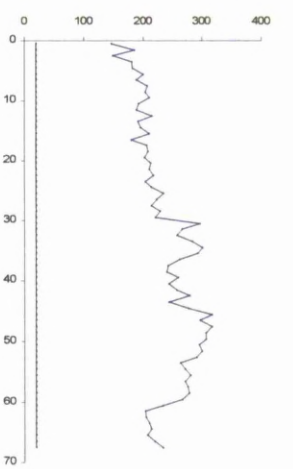


Fig 10r: Pb µg/g



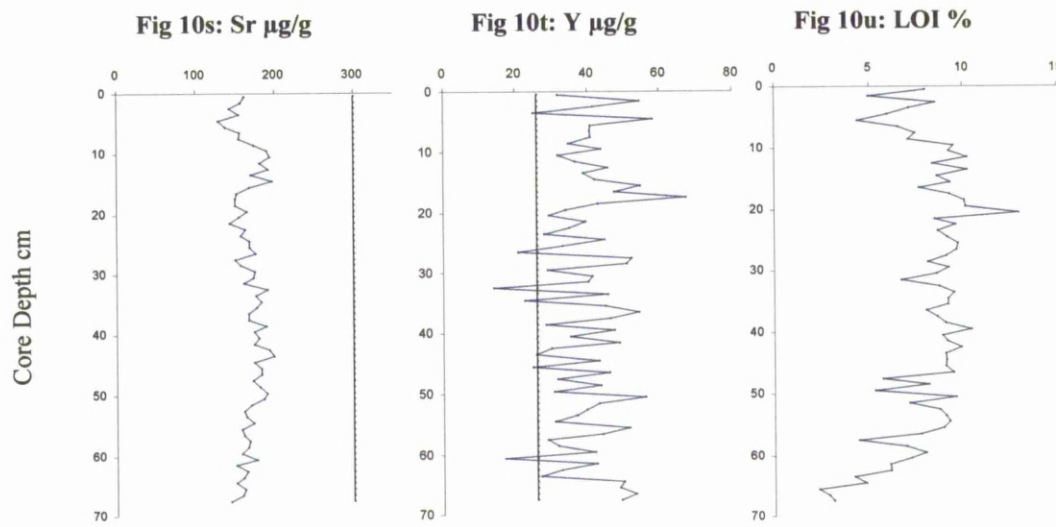


Figure 10a-u: Upper Marsh Core Element Concentrations (Average Shale Values (ASV) are shown in black for comparison with potential natural background concentrations, the data shown in blue are from the upper marsh sediments).

5.3 Upper Marsh Core Magnetics Data

Magnetic Susceptibility (χlf) (Fig 11a) and SIRM (Fig 11b) show a slight decrease in the top layers of the core (0-21cm depth) followed by an overall increase downcore.

χARM (Fig 11c), χARM/SIRM (Fig 11d) and χARM/χlf (Fig 11f) show an increase from the surface followed by a decrease to 13cm depth. There is then a spike in values around 15cm depth, followed by a gradual increase to 29cm after which values remain fairly consistent down to 57cm when they start to show a gradual decrease.

SIRM/ χlf (Fig 11e) values are consistent downcore except for a peak at 24cm.

HIRM (Fig 11g) shows a slight downcore increase.

Hard % (Fig 11h) shows a downcore increase to 21cm followed by a slight decrease to 31cm when values settle down and remain fairly constant. The increase in Hard % (the haematite / goethite contribution) is at the expense of the magnetic contribution from soft remanence (i.e. magnetite). The relative contribution of Hard % to the

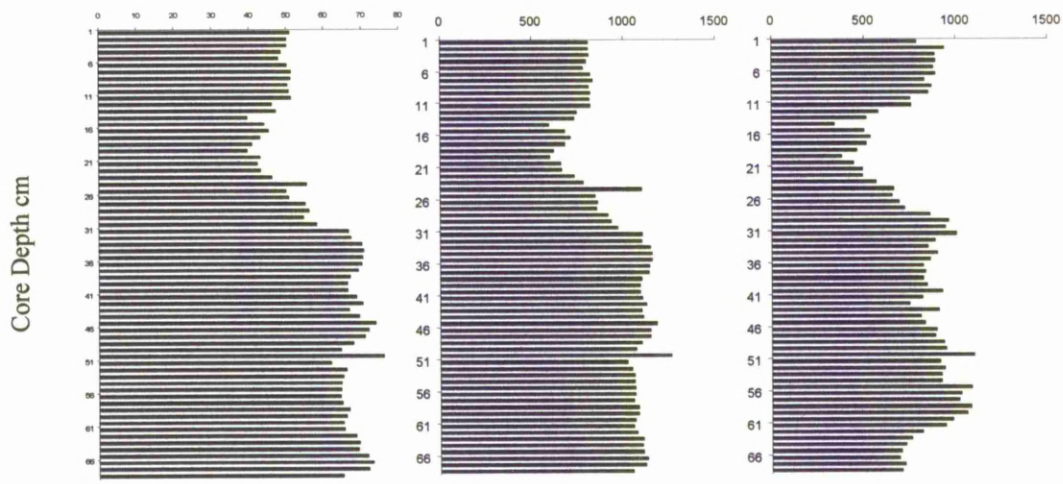
overall magnetic concentration increases as the proportion of soft remanence decreases.

Soft (Fig 11i) values show an overall gradual increase downcore. They also co-vary with χlf and SIRM indicating that the main contribution to the magnetic concentrations is from soft remanence, i.e. magnetite.

FD% (Fig 11j) fluctuates around a central value of 2.5 except for a large peak at 52cm depth.

IRM reverse values (Fig 11k) are relative constant downcore, showing no evidence of backfield divergence.

The results suggest a possible cyclicicity in magnetic grain size with χARM/SIRM and χARM /χlf having higher values when the magnetic grain size is smaller.



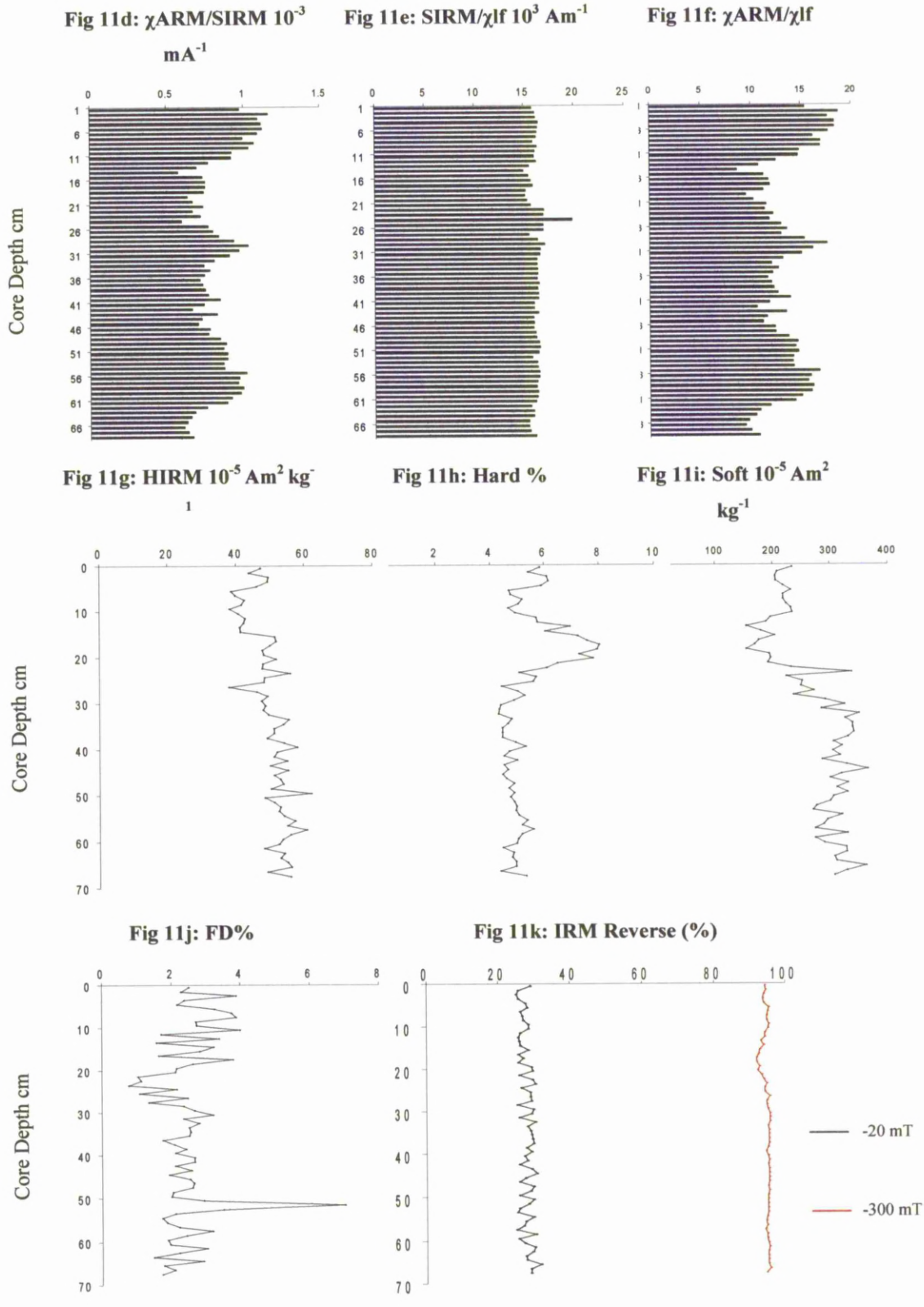


Figure 11a-k: Upper Marsh Core Magnetics Data.

5.4 Upper Marsh Core PCB Data

PCB concentrations (Figure 12a-u) fluctuate markedly downcore, but there appears to be several coincident major peaks in the concentration of most congeners at 7cm, 12cm, 23cm, 47cm, 53cm, and 64cm. Values are high but correspond to concentrations found by other authors (Vane *et al.*, 2003) in the area.

Fig 12a: PCB 18 ng/g

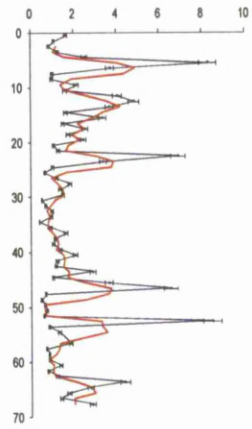


Fig 12b: PCB 28 ng/g

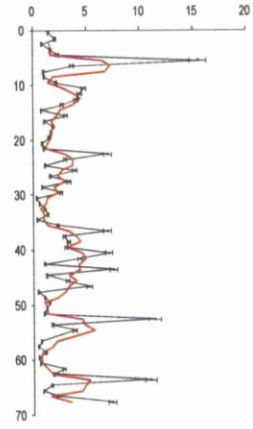
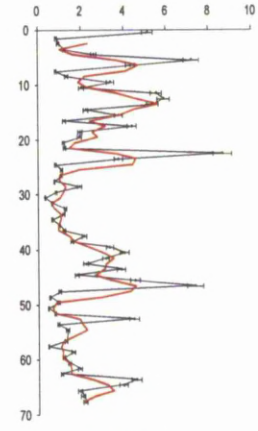


Fig 12c: PCB 52 ng/g



Core Depth cm

Fig 12d: PCB 44 ng/g

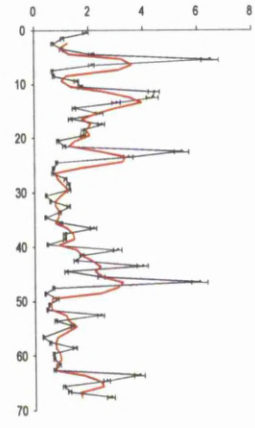


Fig 12e: PCB 47 ng/g

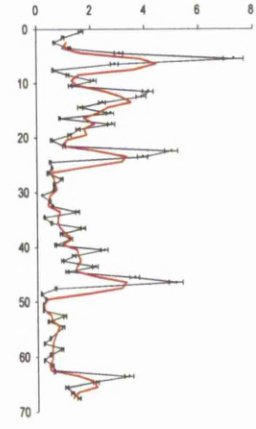
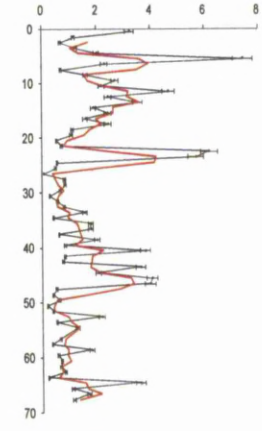


Fig 12f: PCB 49 ng/g



Core Depth cm

Fig 12g: PCB 66 ng/g

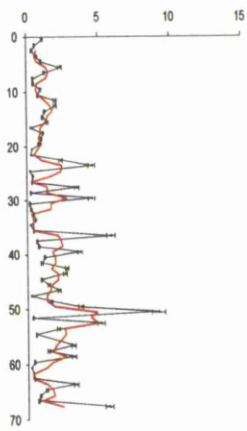


Fig 12h: PCB 101 ng/g

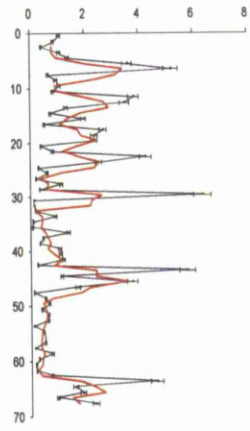


Fig 12i: PCB 105 ng/g

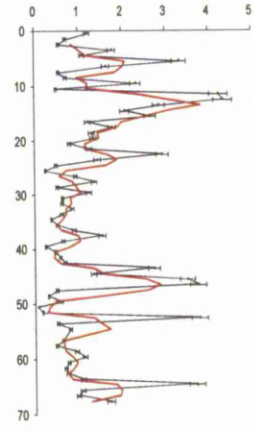


Fig 12j: PCB 118 ng/g

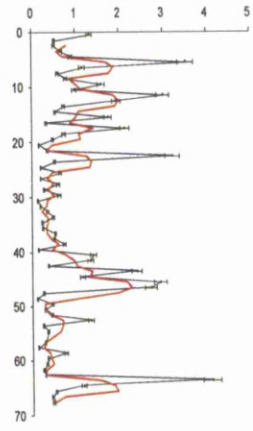


Fig 12k: PCB 128 ng/g

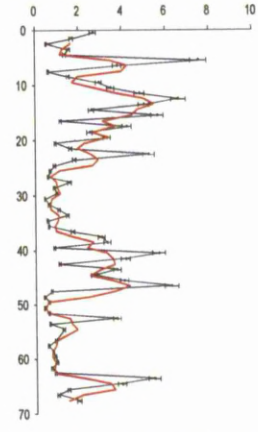


Fig 12l: PCB 138 ng/g

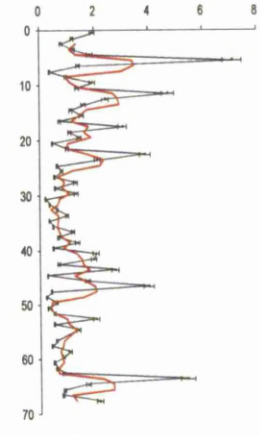


Fig 12m: PCB 141 ng/g

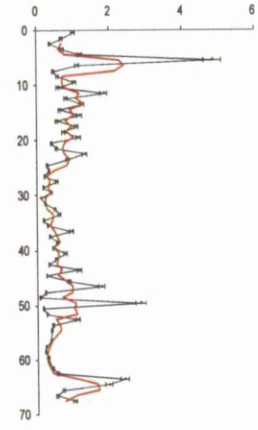


Fig 12n: PCB 151 ng/g

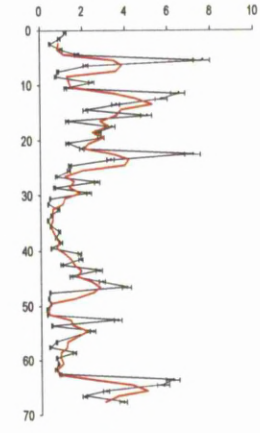
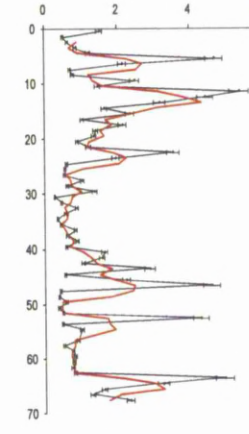


Fig 12o: PCB 153 ng/g



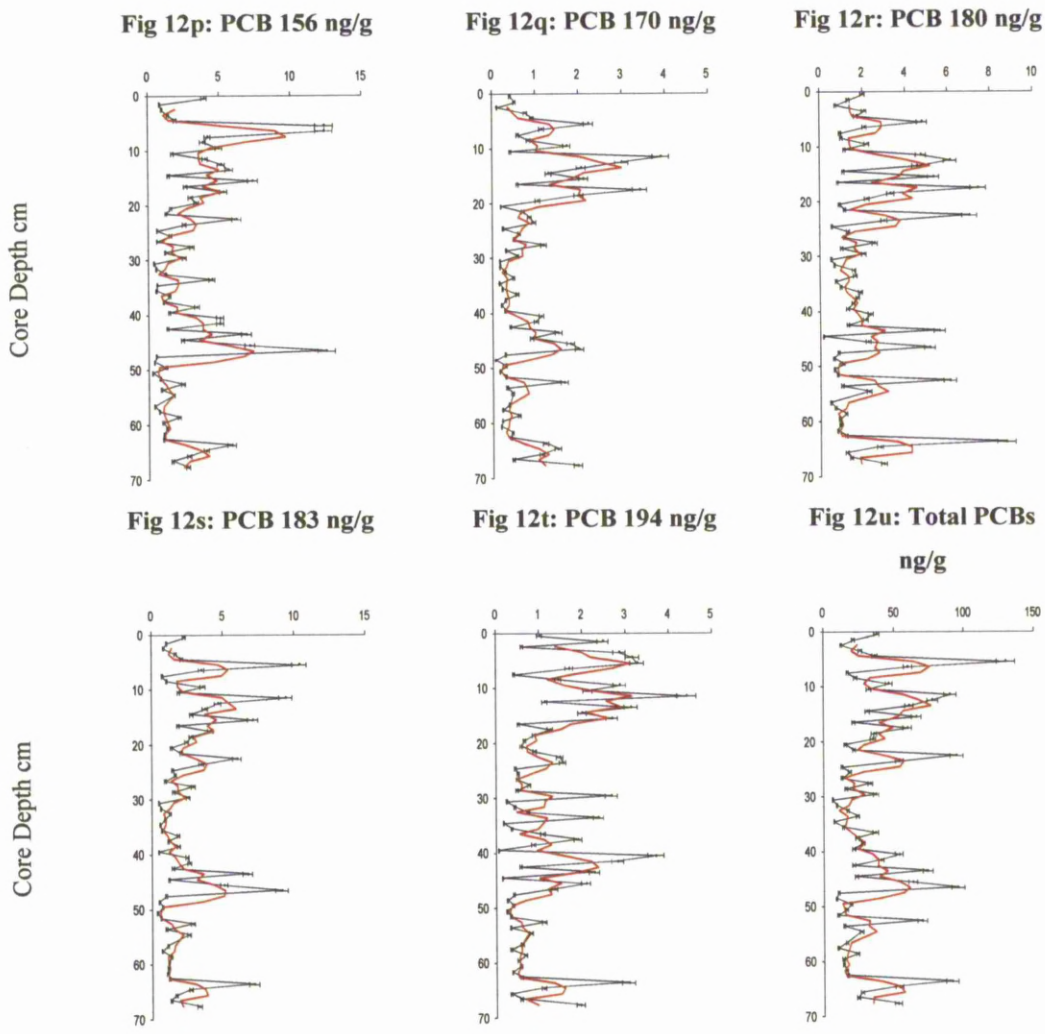
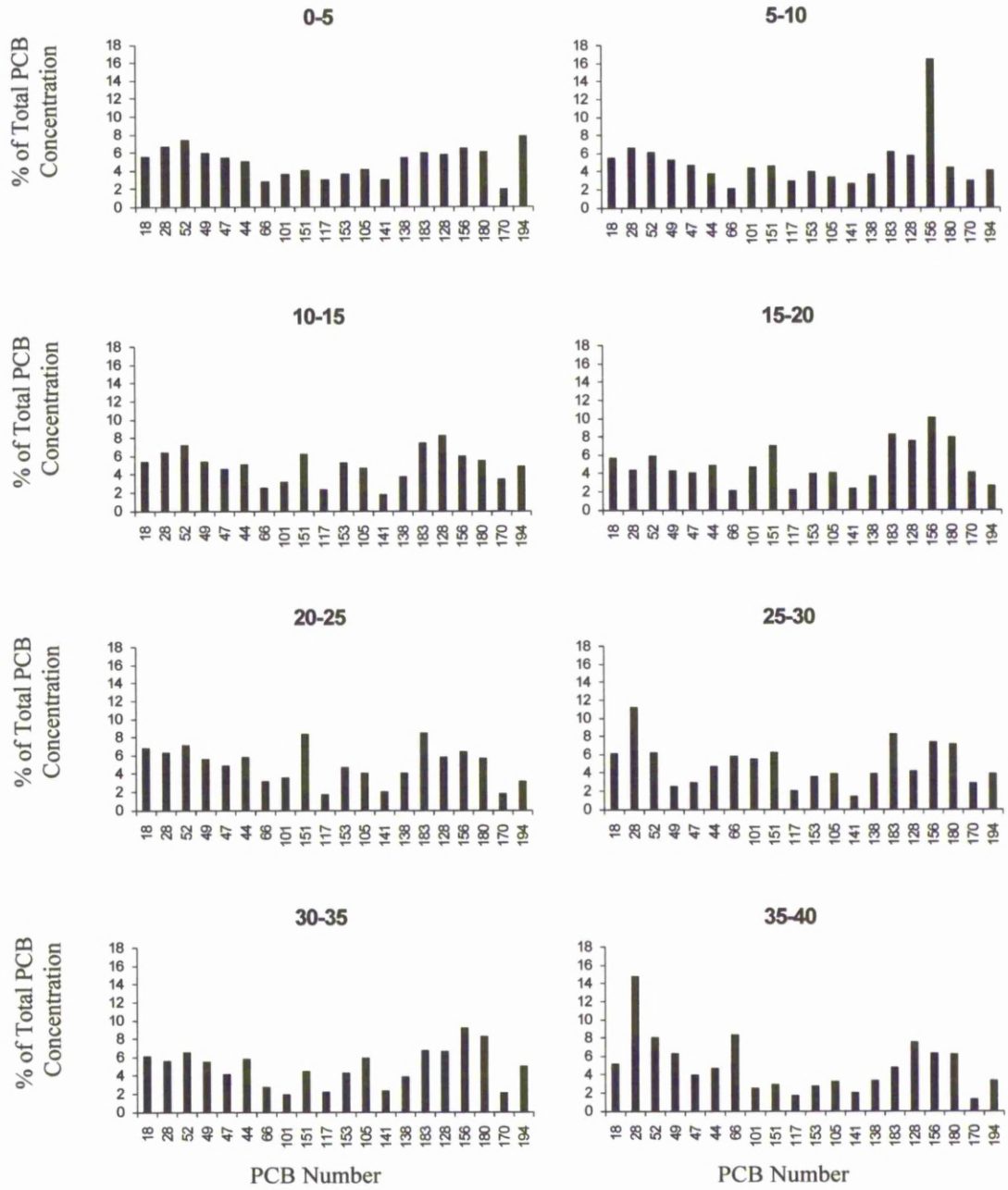


Figure 12a-u: Upper Marsh Core PCB Concentrations. PCB concentrations are shown in black and the general downcore trends can be seen as a 3-point running mean in red.

Figure 13 shows the downcore 5cm combined sample mean distribution of PCB congeners.

Figure 14 shows the mean 5cm combined % distribution of the PCB chlorinated groups which are dominated by the tri, tetra and hexa chlorinated congeners.


0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
% of Total PCB Concentration
PCB Number
18 28 52 49 47 44 66 101 151 117 153 105 141 138 183 128 156 180 170 194

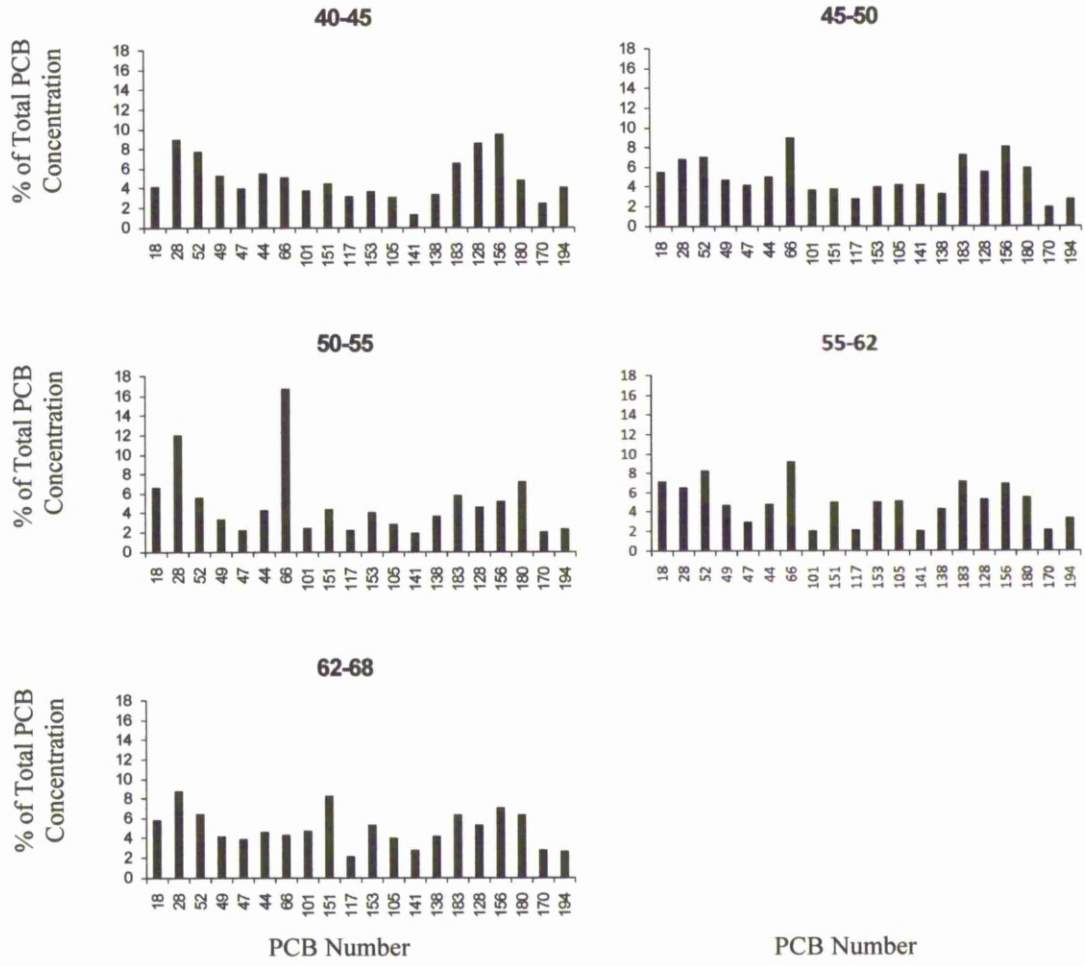


Figure 13: Downcore % Variation of PCB congeners. Values were calculated by combining a number of downcore sections and calculating mean % of the Total PCB concentration of each congener.

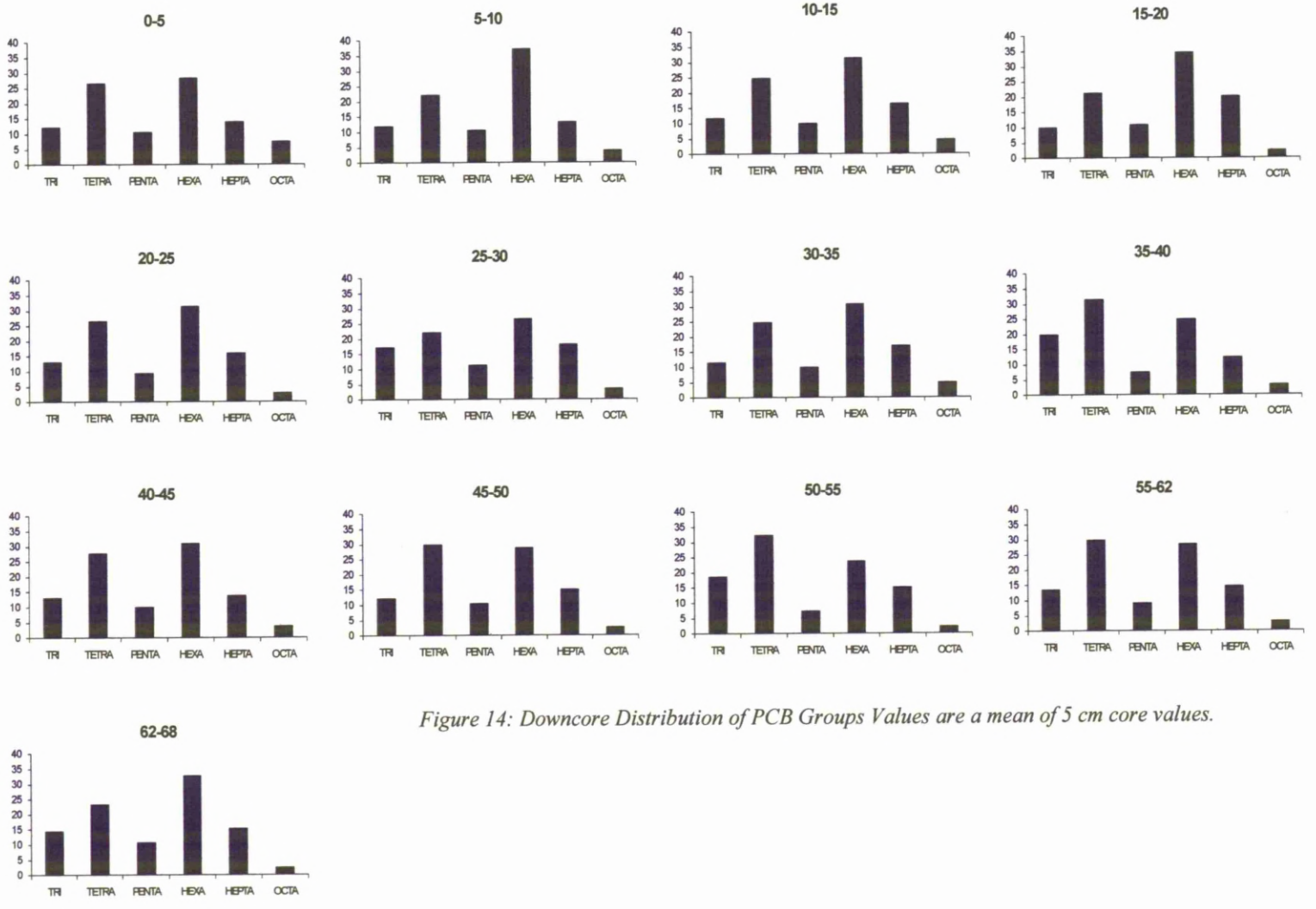


Figure 14: Downcore Distribution of PCB Groups Values are a mean of 5 cm core values.

5.5 Upper Marsh Core PAH Data

5.5.1 PAH downcore distributions

Figure 15a-o show the downcore PAH distribution. As with the PCB data, PAH concentrations fluctuate markedly downcore with several coincident peaks in concentration occurring at 23cm, 30cm, 35cm, 48cm, 52cm and 63cm.

Figure 16 shows the mean 5cm core depth percentage distribution of PAHs which are dominated by the higher molecular weight PAHs.

Fig 15a Acenaphthene µg/g

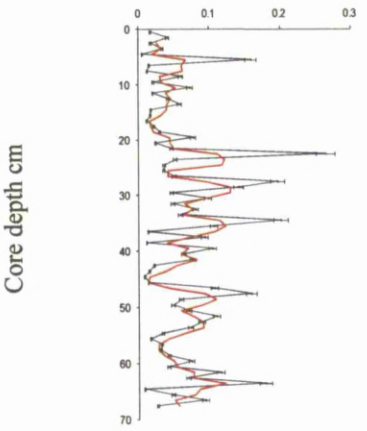


Fig 12b Fluorene µg/g

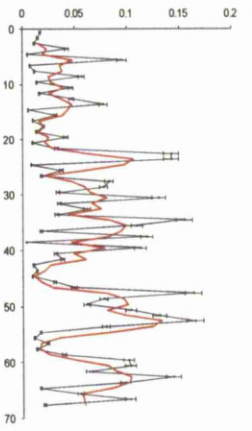


Fig 15c Phenanthrene µg/g

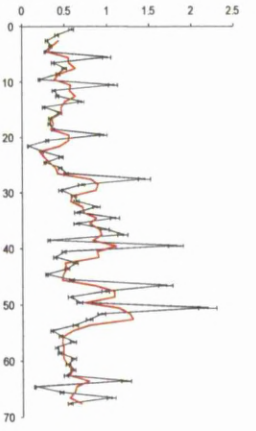


Fig 15d Anthracene µg/g

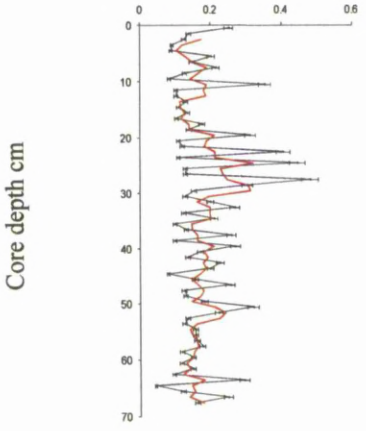


Fig 15e Fluoranthene µg/g

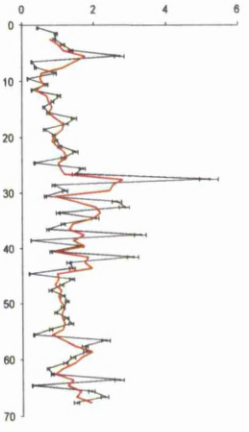
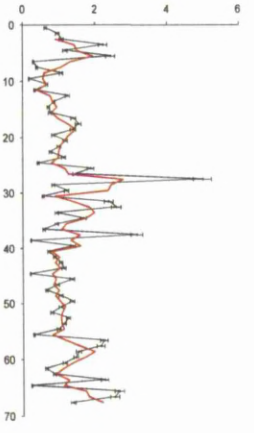


Fig 15f Pyrene µg/g



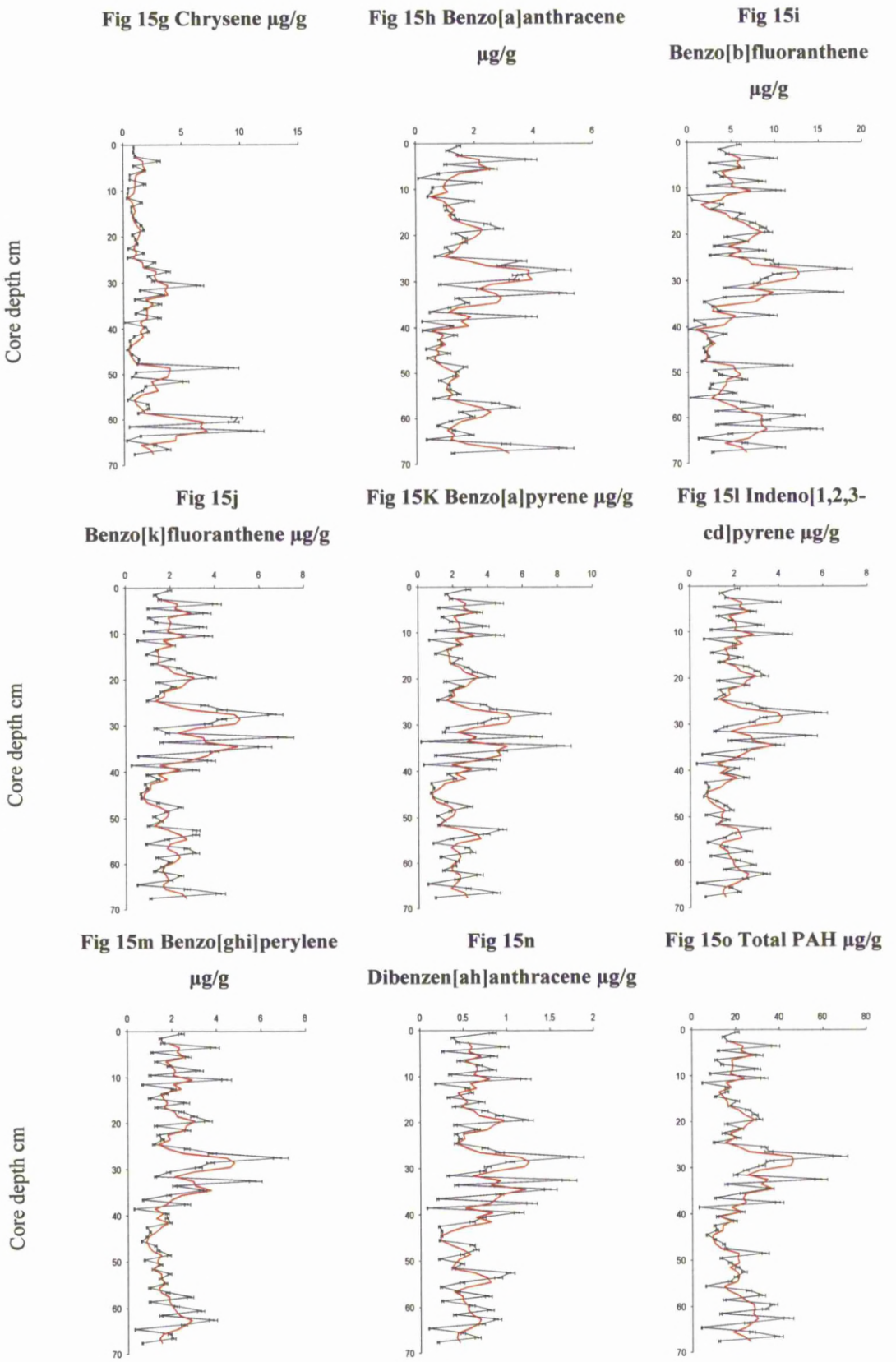
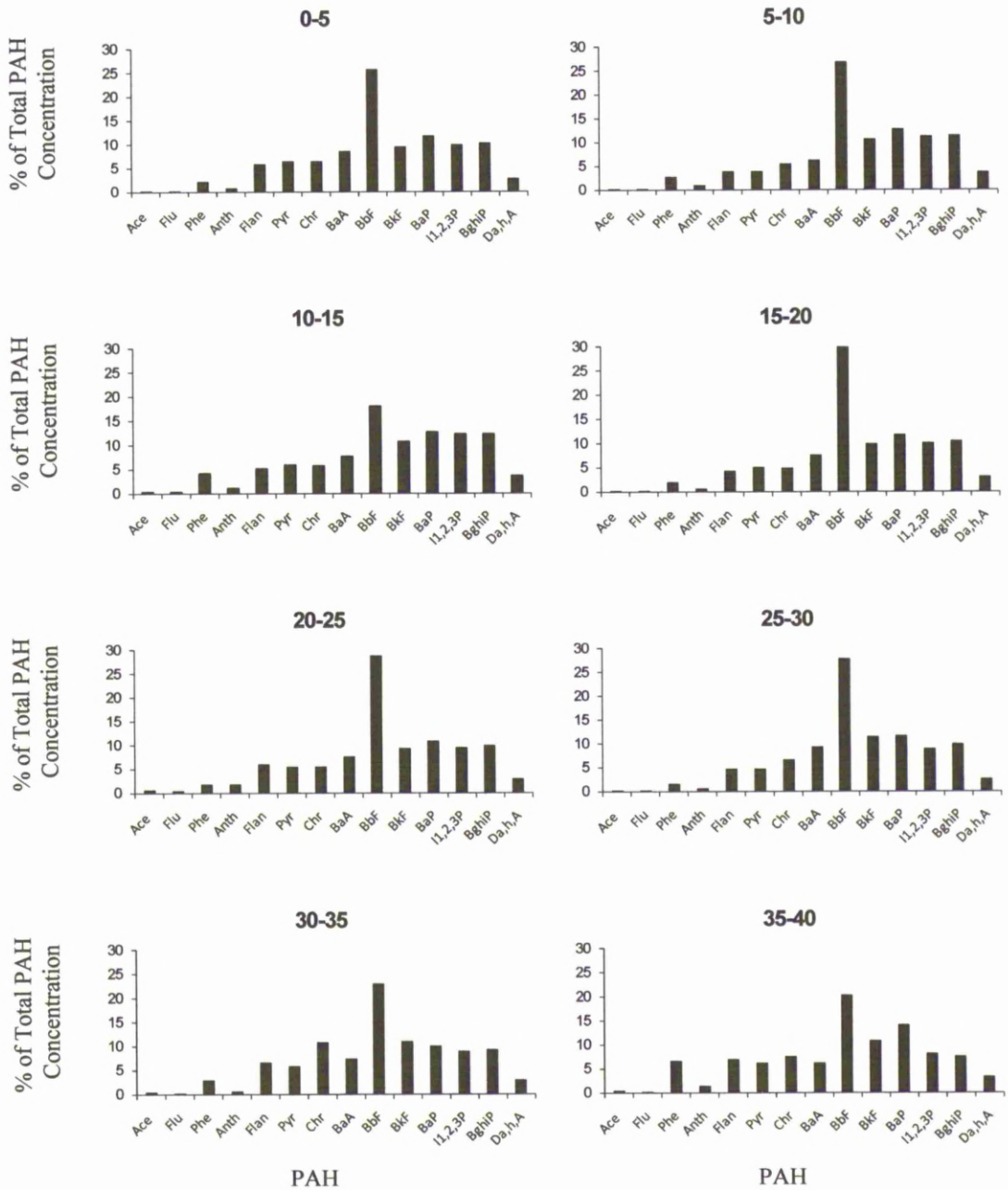


Figure 15a-o: PAH concentrations are shown in black and the general downcore trends can be seen as a 3-point running mean in red.


0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
% of Total PAH Concentration
0
5
10
15
20
25
30
Ace
Flu
Phe
Anth
Flan
Pyr
Chr
BaA
BbF
BkF
BaP
I1,2,3P
BghiP
Da,h,A
PAH

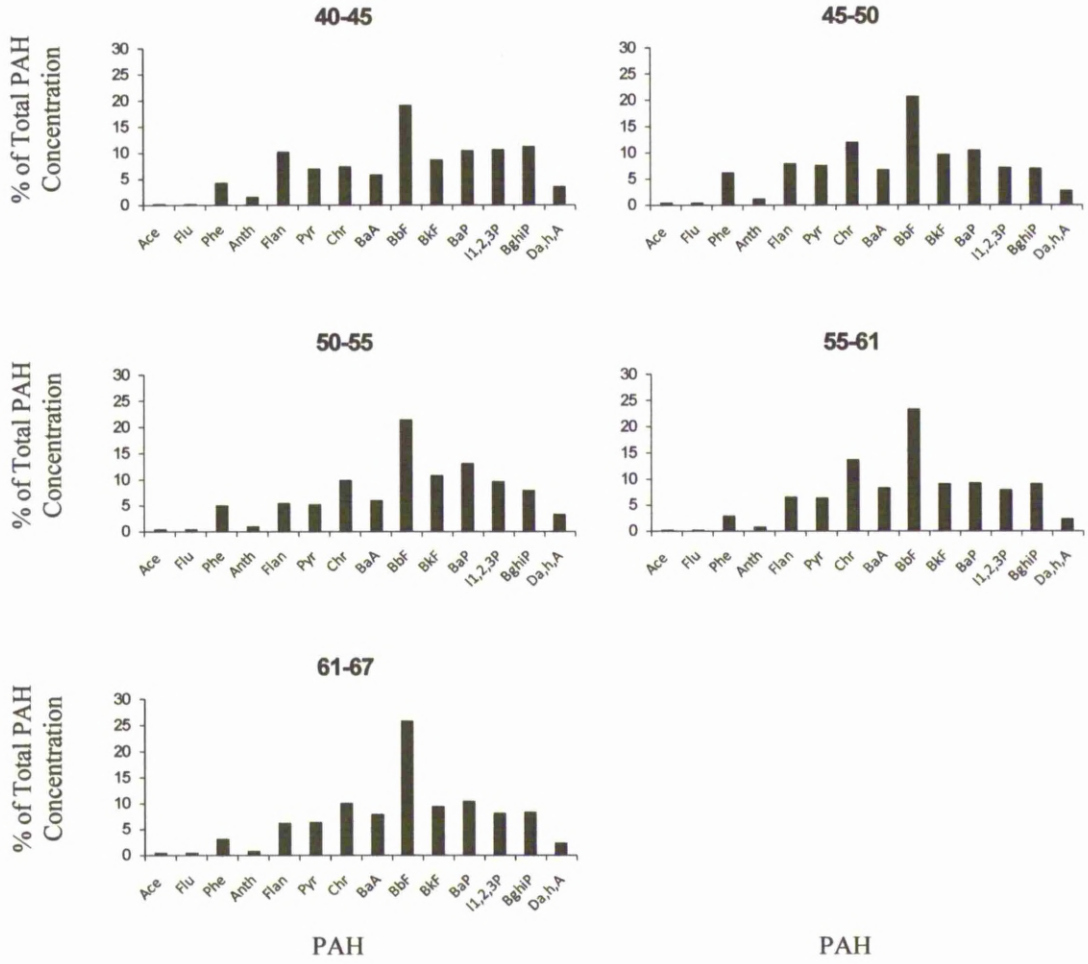


Figure 16: % downcore distribution of PAHs. Values were calculated by combining a number of downcore sections and calculating mean % of the Total PAH concentration of each individual PAH.

5.5.2 PAH ratios

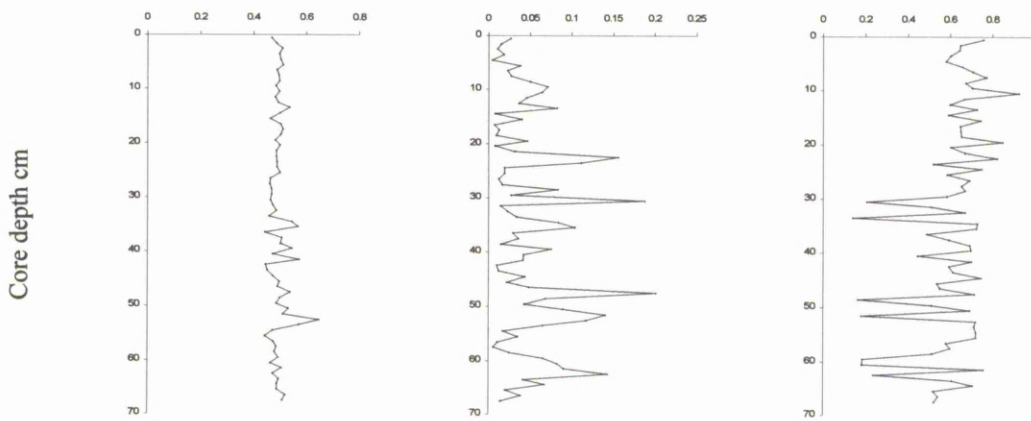
PAH ratios (Figure17a-i) have been used to in an attempt to identify the potential sources of PAHs in the environment (see ratios above for the breakdown of ratio meanings).

The Indeno[1,2,3-cd]pyrene/ (indeno[1,2,3,-cd]pyrene + Benzo [ghi] perylene) ratio is fairly stable downcore except for a few small peaks at 33cm, 42cm and 52cm. Fluorene/(Fluorene + Pyrene) fluctuates downcore with peaks at 22cm, 32cm, 48cm, 52cm and 63cm. Benzo[a]pyrene/ (Benzo[a]pyrene + Chrysene) fluctuates downcore with several lower concentrations recorded at 30cm, 33cm, 48cm, 52cm, 60cm and 62cm. Fluoranthene/Pyrene is fairly stable downcore except for peaks at 23cm and 42cm. Benzo[b]fluoranthene/ Benzo[k]fluoranthene fluctuates downcore with several major peaks at 24cm, 30cm, 37cm, 49cm, 52cm, 59cm and 64cm. Benzo[a]pyrene/ Benzo[ghi]perylene is fairly stable in the top part of the core but fluctuate in the bottom part of the core with a large decrease at 33cm and peaks at 36cm, 40cm, 48cm, 53cm and 66cm. Pyrene/Benzo[a]pyrene is fairly stable downcore with the exception of a large peak at 33cm. Indeno[1,2,3-cd]pyrene/Benzo[ghi]perylene fairly stable in the top part of the core but fluctuate in the bottom part of the core with peaks at 36cm, 41cm, and 53cm CPAH/TPAH shows a fairly steady downcore trend.

Fig 17a Indeno[1,2,3-cd]pyrene/ indeno[1,2,3,-cd]pyrene + Benzo [ghi] perylene

Fig 17b Fluorene/Fluorene + Pyrene

Fig 17c Benzo[a]pyrene/ Benzo[a]pyrene + Chrysene



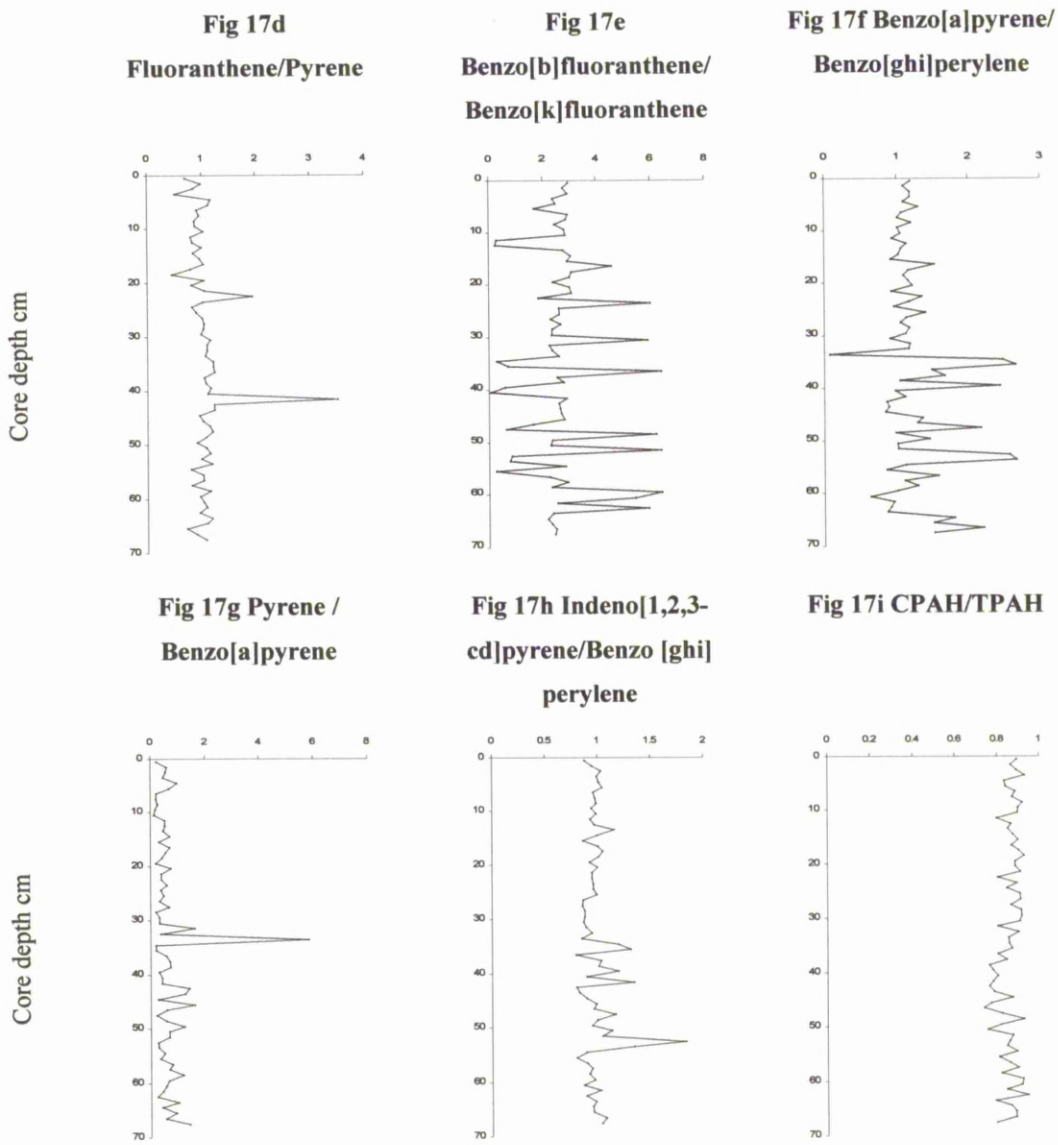


Figure 17: PAH ratios

CPAH = sum of No-alkylated compounds (Fluorene + Pyrene + Benzo[a]anthracene + Chrysene + Benzo[b]fluoranthene + Benzo[k]fluoranthene + Benzo[a]pyrene + indeno[1,2,3-cd]pyrene + benzo[ghi/perylene.

5.6 Upper Marsh Core Organic Matter Data

TOC % (Figure 18a) is an indication of the levels of organic carbon in the sediment and C/N is a ratio showing how the levels of organic carbon and nitrogen change with depth. TOC % shows a similar profile (although with less fluctuation) to LOI, except for in the first 5cm where it shows a downcore increase and LOI shows a decrease. It also shows a peak at 14cm that is not present in LOI. C/N ratio (Figure 18b) shows an overall downcore increase.

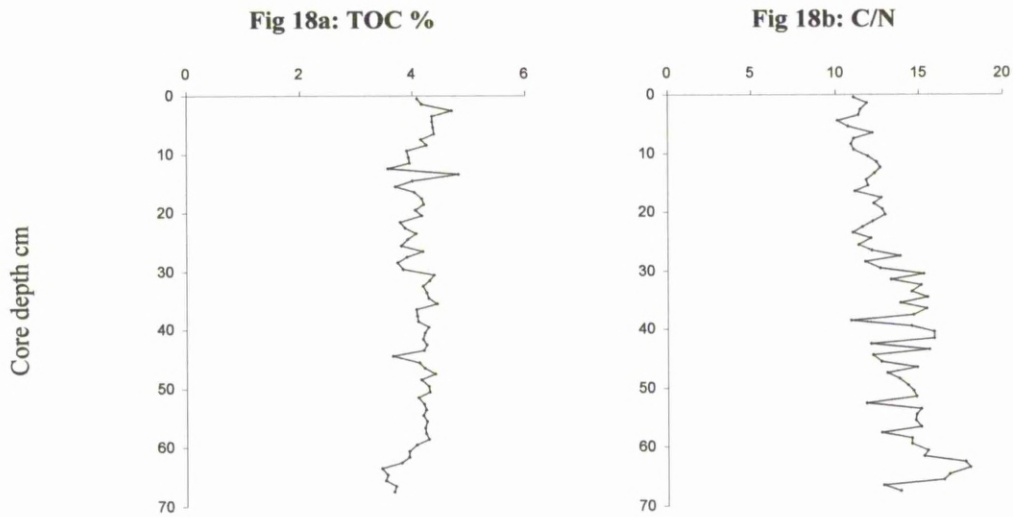


Figure 18: Upper Marsh Core TOC and C/N data.

5.7 Upper Marsh Core Correlations

Positive and negative correlations were considered at both 0.01 and 0.05 levels of significance. SPSS highlighted both strong correlations and those with a weaker but significant link. Correlations were taken to be important if they were over 0.7 (or less than -0.7), i.e. 49% or more of the variance could be explained by the correlation. However, weaker correlations (under 0.7 and above -0.7) that have been highlighted by SPSS as showing a significant relationship within the data have also been discussed.

5.7.1 Upper Marsh Core Element Correlations (See appendix 1 for values)

Si shows a weak positive correlation at the 0.01 significance levels with the Ti, Rb, χlf, SIRM, SIRM/ARM, Soft, -20mT, -300mT, % mud, % coarse silt and kurtosis, a strong positive correlation with Al, Zr, Ca and % very coarse silt, a weak negative correlation with Fe, Br, Rb, LOI, χARM/SIRM, χARM/χlf, Hard %, % sand, % medium sand, % fine sand, % fine silt, % very fine silt, Sorting and TOC and a strong negative correlation with Cl and skewness. At the 0.05 significance level Si shows a weak positive correlation with Cd and HIRM and a weak negative one with K, Mn, Ni, % coarse sand and % medium silt.

Al shows a weak positive correlation at the 0.01 level with Ti, Zr, χlf, SIRM, HIRM, SIRM/ARM, Soft, -20mT, % mud, % very coarse silt, % coarse silt and a strong positive correlation with Si. It shows a weak negative correlation at the 0.01 level with Fe, Cl, Br, Rb, Ni, χARM/SIRM, χARM/χlf, Sorting, skewness, % sand, % coarse sand, % medium sand and % fine sand. It also shows a weak positive correlation at the 0.05 level of significance with Zn, Cd, -300mT, kurtosis and fluoranthene and a weak negative one with Mn, Hard %, mean grain size and % very coarse sand.

Ti shows a weak positive correlation with Si, Al, Ca, K, Zr and % very coarse sand and a weak negative one with Rb, LOI, skewness and TOC at the 0.01 significance level. At the 0.05 level of significance it shows a weak positive correlation with χlf, SIRM, HIRM, Soft, kurtosis and % coarse silt and is a weak negative one with Br.

Ca shows a weak positive correlation with Al, Ti, S, Pb, Zn, Zr, Sr, Cd, Hg, HIRM, SIRM/ARM -20mT, -300mT, kurtosis and % mud, a strong positive one with Si, χlf, SIRM, Soft, % very coarse silt, % coarse silt, a weak negative correlation with Fe, Mn, Cl, Cr, χARM/SIRM, χARM/χlf, Hard %, mean grain size, % sand, % coarse sand, % medium sand and a strong negative one with Br, Sorting, skewness and % fine sand at the 0.01 significance level. At the 0.05 significance level it shows a weak positive correlation with % clay and phenanthrene and weak negative one with Rb, PCB 47, % very coarse sand and TOC.

K shows a weak positive correlation at the 0.01 level with Ti, Fe, S, Cl, % medium sand, % fine silt, % very fine silt, % clay and a weak negative correlation with Zr and mean grain. At the lower 0.05 significance level it shows a weak positive correlation with Si, Pb, Zn and Rb and weak negative one with PCB 138, PCB 156, PCB 194 and % coarse sand.

Fe shows a weak positive correlation at the 0.01 level with K, Mn, Cl, Br, χARM/SIRM, χARM/χlf, Skewness, % fine sand, % fine silt and a weak negative one with Si, Al, Ca, Zr, HIRM, SIRM/ARM, % very coarse silt, % coarse silt. At the 0.05 significance level it shows a weak positive correlation with Cr, FD%, χARM, SIRM/χlf, ARM and % very fine sand and weak negative one with χlf, Soft, -20mT and % very fine silt.

Mn shows a weak positive correlation (at the 0.01 level) with Fe, Br, χARM/SIRM, χARM/χlf, mean grain size, sorting, skewness, % sand, % very coarse sand, % medium sand, % fine silt. It also shows a weak negative correlation with Ca, HIRM, SIRM/ARM, % mud, % very coarse silt and % coarse silt. At the 0.05 level of significance it shows a weak positive correlation with % FD, χARM, ARM and TOC and a weak negative one with Si, Al, Zr, Cd, PCB 156 and kurtosis.

S shows a weak positive correlation, at the 0.01 level, with Ca, K, Cl, Pb, Zn, Sr, Cd, Hg, χlf, SIRM, χARM, SIRM/χlf, HIRM, ARM, Soft, -300mT, PCB 66, kurtosis, % mud, % coarse silt, % medium silt, % very fine silt, % clay and a weak negative one with Br, Hard %, PCB 194, mean grain size, sorting, skewness, % sand, % coarse sand, % medium sand and % fine sand. It also shows a weak positive correlation at the 0.05 level with LOI and % fine silt and a weak negative one with PCB 47, PCB 151, PCB 153, PCB 138, PCB 128 and PCB 170.

At the 0.01 significance level Cl shows a weak positive correlation with K, Fe, S, Br, Rb, LOI and skewness, it also shows a weak negative correlation with Al, Ca, Zr, χlf, and % very coarse silt and strong negative one with Si.. At the lower level of significance (0.05) it shows a weak positive correlation with Pb, Cr, Ni, HARD %, Sorting, % fine silt, % very fine silt and a weak negative one with SIRM, Soft, -300mT and % coarse silt.

Pb is shows a strong positive correlation at the 0.01 level with Zn, % clay and SIRM and a weak positive one with Ca, S, Sr, Cd, Hg, χlf, χARM, HIRM, ARM, Soft, LOI, kurtosis, % mud, % coarse silt, % medium silt, % fine silt, % very fine silt. It shows weak negative correlations with Br, Hard % PCB 151, PCB 194, mean grain size, % coarse sand, % medium sand, % fine sand and % sand. At the 0.05 level of significance it shows a weak positive correlation with K, Cl and % very coarse silt and a weak negative one with PCB 47, PCB 101, PCB 138, PCB 170 and % very fine sand.

Zn shows strong positive correlations at the 0.01 level with Pb, χlf, SIRM, Soft, % mud, % coarse silt, % clay and weak positive correlations with Ca, S, Sr, Cd, Hg, χARM, ARM, HIRM, -300mT, kurtosis, % very coarse silt, % medium silt, % fine silt, % very fine silt and Fluorene. It shows a weak negative correlation with Br, Hard %, PCB 52, PCB 47, PCB 151, PCB 153, PCB 138, PCB 183, PCB 128, PCB 170, PCB 194, total PCB, Sorting, Skewness, % coarse sand, % medium sand and % very fine sand and strong negative one with Mean grain size, % sand, and % very fine sand. At the 0.05 level of significance it shows a weak positive correlation with Al, K, -20mT, phenanthrene and chrysene and a weak negative one with PCB 18, PCB 49, PCB 44, PCB 101, PCB 118, PCB 105, PCB 141, PCB 156 and PCB 180.

Br shows a weak positive correlation at the 0.01 level with Fe, Mn, Cl, Ni, χARM/SIRM, χARM/χlf, Hard %, PCB 194, mean grain size, % sand, % very coarse sand and TOC. It shows strong positive correlations with Sorting, skewness, % coarse sand, % medium sand and % fine sand. Br exhibits weak negative correlations with Si, Al, S, Cu, Pb, Zn, Zr, Cd, Hg, HIRM, SIRM/ARM, -20mT, -300mT, kurtosis, % mud, fluorene and a strong negative correlation with Ca, χlf, SIRM, Soft, % very coarse silt, % coarse silt and clay. At the 0.05 level of significance it shows a weak positive correlation with Rb and PCB 47 and a weak negative one with Ti, % medium silt, % very fine silt, fluoranthene and Chrysene.

Zr shows a weak positive correlation at the 0.01 level with Al, Ti, Ca, χlf, SIRM, SIRM/ARM, soft, -20mT, -300MmT, kurtosis and % coarse silt, a strong positive correlation with Si and % very coarse silt and weak negative one with K, Fe, Cl, Br

Rb, Ni, LOI, χARM/SIRM, χARM/χlf, sorting, skewness, % medium sand, % fine sand, % fine silt, % very fine silt and TOC. At the 0.05 level it shows a weak positive correlation with Cd, % mud, % very fine sand, Fluorene, Pyrene, Benzo[a]anthracene, Benzo[k]fluoranthene, Benzo[a]pyrene and a weak negative one with Mn, % sand, % coarse sand, % medium silt and % clay.

Rb shows a weak positive correlation at the 0.01 level with Cl and Skewness and a weak negative correlation with Si, Al, Ti, Zr and % very coarse silt. At the 0.05 level it shows a weak positive correlation with K, Br, LOI, χARM/χlf, HARD %, % fine silt and TOC and it a weak negative one with χlf, Ca, -20mT and -300mT.

Sr shows a weak positive correlation with Ca, S, Pb, Zn, LOI, χlf and -300mT and it has weak negative correlations with Y, Hard %, mean grain size, sorting, % very coarse sand, % coarse sand and % medium sand at the 0.01 level. It shows a weak positive correlation with Hg, SIRM, Soft, kurtosis, % mud, % coarse silt and % clay and a weak negative one with Skewness and % sand at the 0.05 level of significance.

Cr is shows a weak positive correlation at the 0.01 level with % medium sand and a weak negative one with Ca. At the 0.05 level of significance it shows a weak positive correlation with Fe, Cl, SIRM/χlf, χARM/χlf, sorting, skewness, % sand and acenaphthene and a weak negative one with PCB 18, PCB 49, PCB 141, % clay, % very coarse silt and % coarse silt.

Ni has weak positive correlations at the 0.01 level with Br and Hard % and a weak negative one with Al, Ca, Zr and -300mT. At the lower level of significance it is shows a weak positive correlation with Cl, LOI and % fine sand and a weak negative one with Si, Cd, χlf, SIRM, Soft and Total PAH.

Y has a weak negative correlation with Sr at the 0.01 level and a weak positive one with PCB 170 at the 0.05 level.

LOI shows a weak positive correlation at the 0.01 level with Cl and Sr and a weak negative one with Si, Ti, Zr, Cd, and χlf. It shows a weak positive correlation with S,

Rb, Ni, Hard % and TOC and a weak negative one with SIRM, χARM, ARM, Soft, -300mT, PCB 141, % very coarse sand and Pyrene at the 0.05 level.

Cd shows weak positive correlations at the 0.01 significance level with Ca, S, Cu, Pb, Zn, Hg, χlf, SIRM, χARM, HIRM, Soft, -300mT, kurtosis, % clay, % very coarse silt, % coarse silt, % medium silt, % medium silt and % very fine silt . At this level of significance it has a weak negative correlation with Br, LOI, Hard %, mean grain size, sorting, skewness, % sand, % coarse sand, % medium sand, % fine sand, % very fine sand and TOC. At the lower 0.05 level of significance it shows a weak positive correlation with Si, Al, Ti, Mn, Zr, -20mT, PCB 66, % fine silt and Chrysene and a weak negative one with Ni and Benzo[ghi]perylene.

Hg shows a weak positive correlation with Ca, S, Cu, Pb, Zn, Cd, χlf, SIRM, χARM, HIRM, ARM, Soft, % mud, % coarse silt, % medium silt, % fine silt, % very fine silt, % clay and a weak negative one with Br, PCB 49, PCB 47, PCB 151, PCB 105, PCB 128, PCB 170, PCB 194, Total PCB, mean grain size, sorting, skewness, % sand, % coarse sand, % medium sand, % fine sand and % very fine sand. At the 0.05 level shows a weak positive correlation with Sr, -300mT, PCB 66, Kurtosis, Phenanthrene and a weak negative one with Hard %, PCB 18, PCB 52, PCB 44, PCB 101, PCB 118, PCB 153, PCB 141, PCB 138, PCB 183, PCB 156 and PCB 180.

5.7.2 Upper Marsh PCB Correlations (See appendix 1)

PCBs correlate well with each (although many of these correlations are weak) and PCB 66 shows the fewest correlations with the other PCBs. Many also show negative correlations with the finer grain size fractions (and magnetic indicators of grain size) and positive correlations with coarser grain size material.

PCB 18 shows a strong positive correlation with PCB 28, PCB 52, PCB 49, PCB 47, PCB 44, PCB 151, PCB 118, PCB 153, PCB 105, PCB 138, PCB 183, PCB 128, PCB 156, PCB 180 and Total PCB and a weak positive one with PCB 101, PCB 141, PCB 170 and PCB 194 at the 0.01 level of Significance. At the 0.05 level it shows a weak positive correlation with PCB 66, % sand, % fine sand, mean grain size, soft

and Acenaphthene and a weak negative one with χARM, ARM, % mud, % coarse silt, % medium silt, % fine silt and % very fine silt.

PCB 28 is shows a weak positive correlation the 0.01 level with PCB 52, PCB 49, PCB 47, PCB 66, PCB 101, PCB 151, PCB 118, PCB 105, PCB 141, PCB 183, PCB 128, PCB 156, PCB 180, PCB 170, PCB 194, a strong positive one with PCB 18, PCB 44, PCB 153, PCB 138 and Total PCB and a weak negative one with % medium silt, % fine silt and % very fine silt. At the 0.05 level it shows a weak positive correlation with Acenaphthene.

PCB 52 shows a weak positive correlation at the 0.01 level with PCB 28, PCB 101, PCB 141, PCB 170, PCB 194, SIRM/ARM, mean grain size and % fine sand and a strong positive one with PCB 18, PCB 49, PCB 47, PCB 44, PCB 151, PCB 118, PCB 153, PCB 105, PCB 138, PCB 183, PCB 128, PCB 156, PCB 180 and Total PCB. It shows a weak negative correlation with χARM, ARM, % medium silt, % fine silt, % very fine silt and Benzo[b]fluoranthene. At the 0.05 level it shows a weak positive correlation with % sand and % very fine sand and a weak negative one with % mud, % coarse silt, % clay, Chrysene and Total PAH.

Total PCB shows a strong positive correlation with PCB 18, PCB 28, PCB 52, PCB 49, PCB 47, PCB 44, PCB 101, PCB 151, PCB 118, PCB 153, PCB 105, PCB1 41, PCB 138, PCB 183, PCB 128, PCB 156, PCB 180, PCB 170, a weak positive one with PCB 194, mean grain size and % sand and a weak negative correlation with χARM, ARM % mud, % medium silt, % fine silt, very fine silt, % clay at the 0.01 level. It shows a weak positive correlation with PCB 66, sorting, % medium sand, % fine sand, % very fine sand and a weak negative one with HIRM, % very coarse silt, Chrysene and Benzo[b]fluoranthene at the 0.05 level.

These trends are repeated amongst the other PCBs

All PCBs apart from PCB 28 and 66 show a negative correlation with Hg. Several PCBs are also negative with Zn (52, 47, 151, 153, 138, 183, 128, 170, 194), Pb (47, 101, 151, 138, 170, 194), Cu (47, 128, 156), Sr, (47, 151, 153, 138, 128, 170) or S (18, 49, 44, 101, 118, 105, 141, 156, 180,194). PCB 49 has negative correlations

with Cr, PCBs 138 and 194 have a negative correlation with K, PCB 156 has a negative correlation with K and Mn. The only PCBs that show positive relationships with the metals are PCB 47 and 194 (Br), PCB 66 (S and Cd), PCB 170 (Y). PCB 18 shows a weak positive correlation with Acenaphthene and PCB 66 shows a weak positive one with Phenanthrene, There are several PAHs that show weak negative correlation with PCBs: Benzo[b]fluoranthene (PCB 52, 49, 47, 44, 153, 105, 128, 156, 170, Total PCB), Chrysene (PCB 52, 49, 47, 44, 151, 153, 183, 128, 156, 170, 194, Total PCB), Total PAH (PCB 52, 49, 47, 44, 153, 128) Benzo[a]anthracene (PCB 49), Benzo[k]fluoranthene (PCB 49).

5.7.3 Upper Marsh Core PAH Correlations (See appendix 1)

As with the PCB correlations PAHs show good correlations amongst themselves (although again some of these are weak).

Acenaphthene shows a weak positive correlation at the 0.01 level with Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1.2.3-cd]pyrene, Benzo[ghi]perylene, Dibenz[a,h]anthracene and a strong one with Fluorene. It shows a weak positive correlation at the 0.05 level with -300mT, % mud, % coarse silt and a weak negative one with Hard %, sorting, skewness, % sand and % fine sand.

Fluorene shows a weak positive correlation at the 0.01 level with Phenanthrene, Chrysene, Benzo[K]fluoranthene, Benzo[a]anthracene, Dibenz[a,h]anthracene, Total PAH, % mud, % coarse silt, Soft and SIRM, a strong positive one with Acenaphthene and a weak negative correlation with % sand. At the 0.05 level it shows a weak positive correlation with Fluoranthene, Benzo[b]fluoranthene, benzo[ghi]perylene, χlf -20 mT, -300mT and a weak negative one with SIRM/χlf, Hard %, mean grain size, sorting, skewness, % medium sand and % fine sand.

Phenanthrene shows a weak positive correlation with χlf, SIRM, Soft, -300mT, Acenaphthene, Fluorene, Anthracene, Fluoranthene, Pyrene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h[anthracene, Total PAHs and % coarse silt and a weak negative one with skewness and Hard % at the 0.01 level. At the 0.05 level of

significance it is shows a weak positive correlation with Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene, % mud, % very coarse silt, % clay and a weak negative one with χARM, mean grain size, % sand, % medium sand and % fine sand.

At the 0.0 1 Level Anthracene shows a weak positive correlation with Acenaphthene, Phenanthrene, fluoranthene, pyrene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene and total PAH. At the 0.05 level of significance it shows a weak positive correlation with Benzo[a]anthracene and benzo[b]fluoranthene.

Fluoranthene shows a weak positive correlation with, Acenaphthene, Phenanthrene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene, Total PAH and a strong positive one with Pyrene at the 0.01 level. It shows a weak positive correlation with Soft, Fluorene and % very coarse silt and a negatively weak one with skewness and % fine sand at the 0.05 level.

At the 0.01 level of significance Chrysene shows a weak positive correlation with Fluorene Benzo[b]fluoranthene, Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene and Total PAH, % mud, % coarse silt, % medium silt and a weak negative one with mean grain size, % sand, % very fine sand, It shows a weak positive correlation with Benzo[a]anthracene, Benzo[a]pyrene, Dibenz[a,h,]anthracene, % fine silt, % very fine silt and % clay and a weak negative one with Sorting and SIRM at the 0.05 level.

Total PAH shows a weak positive correlation with Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Chrysene and a strong positive one with Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1.2.3-cd]pyrene, Benzo[ghi]perylene, Dibenz[a,h,]anthracene and Pyrene at the 0.01 level.

TOC shows a weak positive correlation with Sorting and Skewness and a weak negative correlation with % very coarse silt at the 0.01 level. It shows a weak

positive correlation with % coarse sand and % medium sand and a weak negative correlation with % coarse silt at the 0.05 level of significance.

There are several metals that show positive correlations with PAHs: Cr (acenaphthene) Zr, (Fluorene, Pyrene, Benzo[a]anthracene, Benzo[k]fluoranthene, Benzo[a]pyrene), Zn (Fluorene), Ca (Phenanthrene), Hg, (Phenanthrene), S (phenanthrene, Chrysene), Cd (Chrysene) and several that show negative ones Cd (Benzo[ghi]perylene), Br, (Chrysene Fluoranthene) and Pyrene is negative with LOI.

5.7.4 Upper Marsh Core Magnetic Correlations (See appendix 1)

χlf shows a weak positive correlation with χARM, HIRM, ARM, -20mT, % clay, mean grain size, kurtosis, a strong positive one with SIRM, soft, -300mT, % very coarse silt, % coarse silt, % mud and weak negative one with % coarse sand, % medium sand and a strong negative correlation with Hard %, % fine sand, sorting, skewness and % sand at the 0.01 level. It shows a weak positive correlation with % medium silt, % very fine silt and weak negative one with % very fine sand at the 0.05 level.

%FD is shows a weak negative correlation with SIRM/χlf and SIRM/ARM at the 0.01 level of significance. At the 0.05 level of significance it shows a weak positive correlation with χARM/SIRM.

SIRM shows a weak positive correlation with χARM, HIRM, ARM, -20mT, % very coarse silt, % clay, kurtosis, a strong positive correlation with χlf, Soft, -300mT, % coarse silt, % mud, a weak negative one with % coarse sand, % medium sand, mean grain size, and a strong negative correlation with Hard %, % fine sand, sorting, skewness and % sand at the 0.01 significance level. At the 0.05 significance level it shows a weak positive correlation with SIRM/χlf, % medium silt, % very fine silt and a weak negative one with % very fine sand.

At the 0.01 level of significance χARM shows a weak positive correlation with χlf, SIRM, χARM/SIRM, SIRM/χlf, HIRM, -300mT, % coarse silt, % medium silt, % fine silt, % very fine silt, % clay, % mud, a strong positive correlation with ARM and Soft. It has a weak negative correlation with Hard %, SIRM/ARM, % fine sand, %

very fine sand, mean grain size, sorting and % sand. It shows a weak positive correlation with % Kurtosis and TOC and a weak negative correlation with % medium sand and skewness at the 0.05 Level.

χARM/SIRM is shows a weak positive correlation with % coarse silt, % fine silt, Sorting Skewness, TOC χARM, and ARM, a strong positive one with χARM/χlf, a weak negative correlation with % very fine sand, % very coarse silt and a strongly negative one with SIRM/ARM at the 0.01 level. It is shows a weak positive correlation with FD%, %medium silt, % very fine silt and a weak negative one with -20mT and % coarse silt at the 0.05 level.

SIRM/χlf shows a weak positive correlation with χARM/χlf and ARM and a weak negative one with FD% at the 0.01 level. At the 0.05 level it shows a weak positive correlation with Soft, -300mT and % medium silt and a weak negative one with Hard %.

χARM/χlf shows a weak positive correlation with % coarse sand, % fine silt, skewness, TOC, χARM, SIRM/χlf and ARM, a strong positive correlation with χARM/SIRM, a weak negative correlation with % very fine sand and % very coarse silt and a strong negative correlation with SIRM/ARM at the 0.01 level of significance. At the 0.05 level it shows a weak positive correlation with % very coarse sand, % medium silt, and % very fine silt and a weak negative one with % coarse silt.

HIRM is shows a weak positive correlation with χlf, SIRM, χARM, Soft, % very coarse silt, % coarse silt, % medium silt, % very fine silt, % clay, kurtosis, % mud SIRM/χlf, -300mT and a weak negative one with % sand, % coarse sand, % medium sand, % fine sand, % very fine sand, mean grain size, sorting, skewness at the 0.01 level. At the 0.05 level it shows a weak positive correlation with % fine silt.

Hard % shows a weak positive correlation with % sand, % fine sand, % medium sand, mean grain size, sorting, skewness, a weak negative one with χARM, ARM, % very coarse silt, % coarse silt, kurtosis, % mud and a strong negative one with χlf,

SIRM, Soft and -300mT. At the 0.05 level it shows a weak positive correlation with % coarse sand and a weak negative one with SIRM/χlf and -20mT.

ARM shows a weak positive correlation with χlf, SIRM, χARM/SIRM, SIRM/χlf, SIRM/χlf HIRM, -300mT, Soft, % coarse silt, % medium silt, % fine silt, % very fine silt, % clay, and % mud, a strong positive one with χARM, a weak negative correlation with Hard %, SIRM/ARM, % sand, % fine sand, % very fine sand, mean grain size and sorting at the 0.01 level. It shows a weak positive correlation with kurtosis and TOC and a weak negative one with % medium sand and skewness at the 0.05 level.

SIRM/ARM shows a weak positive correlation with % very fine sand, % Very coarse silt, a weak negative one with % medium silt, % fine silt, % very fine silt, skewness, TOC, χARM, %FD and ARM and a strong negative correlation with χARM/SIRM and χARM/χlf at the 0.01 level. It shows a weak positive correlation with -20mT and a weak negative one with % coarse sand, % medium sand and sorting at the 0.05 level.

At the 0.01 level of significance Soft shows a weak positive correlation with % clay, kurtosis, χARM, ARM, HIRM, and -20mT and a strong one with χlf, SIRM, -300mT, % very coarse silt, % coarse silt and % mud. It shows a weak negative correlation with Hard %, % coarse sand, % medium sand, mean grain size and a strong negative one with % fine sand, sorting, skewness and % sand. At the 0.05 level it shows a weak positive correlation with SIRM/χlf and % medium sand.

-20mT exhibits a weak positive correlation with χlf, SIRM, Soft, % coarse silt, % very coarse silt and a weak negative one with % fine sand, Sorting and skewness at the 0.01 level At the 0.05 level it shows a weak positive correlation with SIRM/ARM, -300mT and % mud and a weak negative one with χARM/SIRM, Hard %, % medium sand and % sand.

-300mT shows a weak positive correlation with χARM, ARM, % very coarse silt, % coarse silt, % mud and kurtosis, a strong positive correlation with χlf, SIRM, and Soft, a weak negative one with % medium sand, % fine sand, % sand, mean grain

size, sorting, skewness and a strong negative correlation with Hard % at the 0.01 level. It shows a weak positive correlation with SIRM/χlf, -20mT and a weak negative one with % coarse sand at the 0.05 level.

5.8 Principal Component Analysis Upper Marsh Core

Multivariate statistical analysis using Principal Component Analysis (PCA) was undertaken in an attempt to establish relationships between organic matter, grain size and pollutant inputs (PCBs, PAHs and heavy metals). The results of this are given below as a series of bivariate plots and associated eigenvectors and eigenvalues.

5.8.1 Upper Marsh Element, Organic Matter and Grain Size PCA

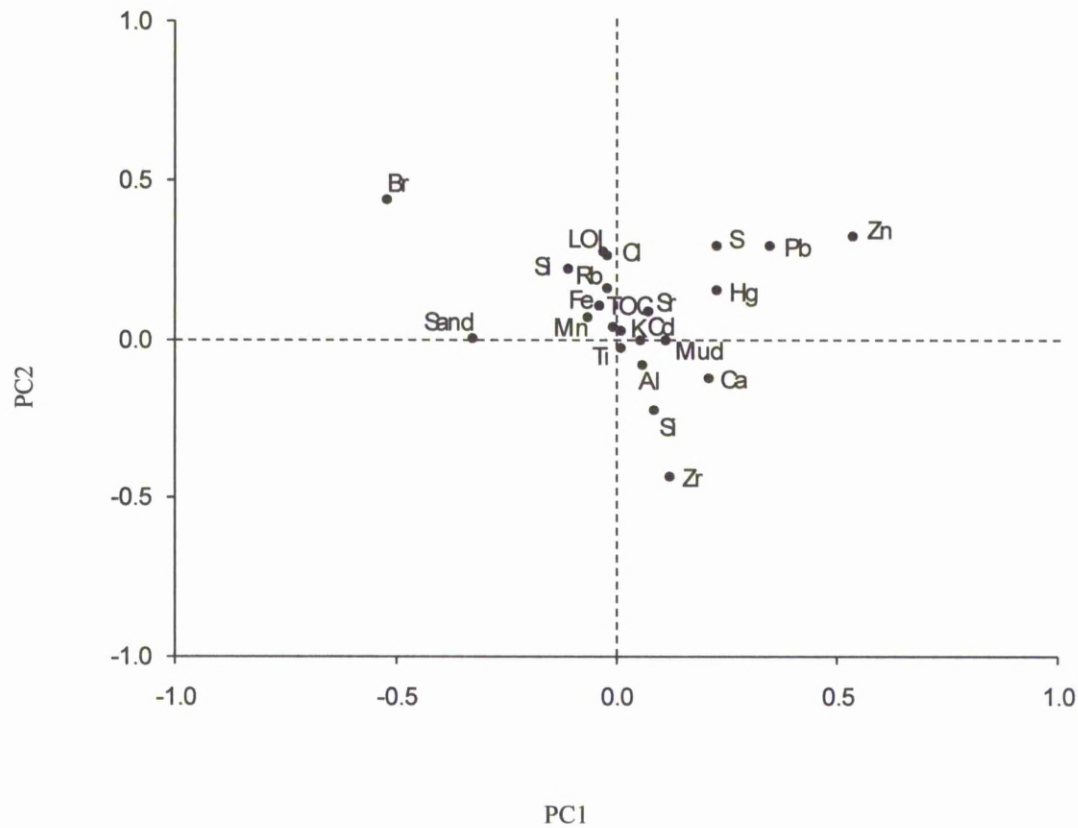


Figure 19: PCA scatter plot of Eigenvectors comparing elements, organic matter and grain size. The relationship between PCA 1 (which explained 51.7% of the total variance) and PCA 2 (which explained a further 21.4%) is shown, along with graphical representations of the contributions of the original variables to both PC 1 and PC 2.

It appears that there are 3 main groupings of parameters in this analysis. Zr, Si, Ca, Al (the lithogenic fraction with a potential bias to coarse grained material), TOC, LOI, Mn, Fe Ni, Br (the organic matter fraction and marine influences?) and Hg, Pb, Zn, S, Sr (those with a possible pollutant input relationship). The first 3 components account for 80% of the variation.

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	0.177	51.7	51.7
2	7.31E-2	21.4	73.0
3	2.47E-2	7.2	80.2
4	1.61E-2	4.7	84.9
5	1.13E-2	3.3	88.2

Eigenvectors

(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Si	0.087	-0.222	0.108	0.062	0.034
Al	0.059	-0.080	0.003	0.074	-0.015
Ti	0.009	-0.025	0.005	-0.020	0.046
Ca	0.209	-0.122	0.192	0.244	-0.048
K	0.008	0.026	-0.020	0.006	0.003
Fe	-0.038	0.110	-0.066	-0.042	0.089
Mn	-0.064	0.070	-0.103	-0.193	0.197
S	0.227	0.295	-0.001	0.520	0.411
Cl	-0.021	0.265	-0.056	0.170	0.059
Pb	0.345	0.293	-0.143	-0.028	0.232
Zn	0.535	0.322	-0.110	-0.219	0.072
Br	-0.523	0.436	-0.141	-0.112	0.057
Zr	0.120	-0.436	0.069	0.157	0.192
Rb	-0.022	0.160	-0.134	-0.035	-0.059
Sr	0.072	0.087	0.144	0.213	-0.053
Ni	-0.112	0.222	0.890	-0.180	0.259
Cd	0.056	-0.003	-0.013	-0.042	0.052
Hg	0.227	0.154	0.149	-0.324	-0.443
LOI	-0.028	0.276	0.133	0.509	-0.603
TOC %	-0.007	0.042	-0.023	-0.014	-0.024
% sand	-0.326	0.003	-0.063	0.243	0.189
% mud	0.114	-0.003	0.029	-0.055	-0.061

5.8.2 Upper Marsh Core PCB, Organic Matter and Grain Size PCA

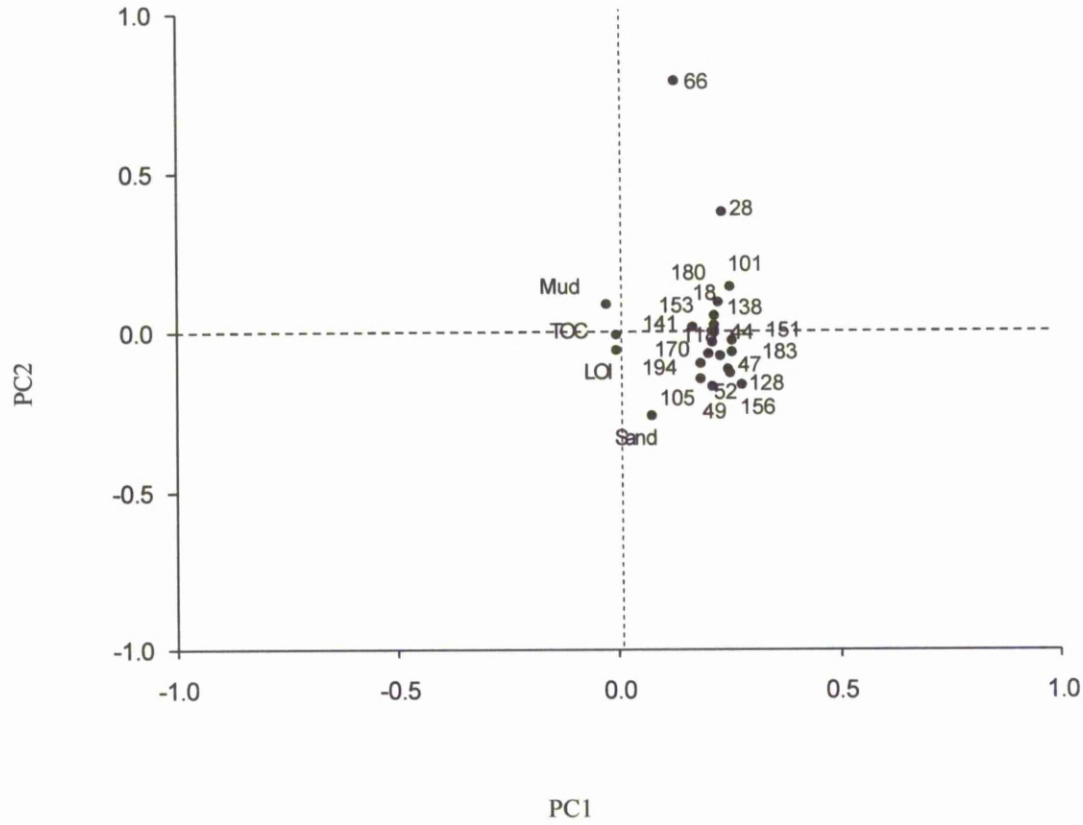


Figure 20: PCA scatter plot of Eigenvectors comparing PCBs, organic matter and grain size. The relationship between PCA 1 (which explained 71.3% of the total variance) and PCA 2 (which explained a further 6.8%) is show. along with graphical representations of the contributions of the original variables to both PC 1 and PC 2.

The first 3 components account for 81% of the variation and there appear to be 2 main clusters of PCBs and a couple of outliers (PCB 28, 66). Neither of these groupings can be explained by congener types (e.g. PCBs with similar ring numbers grouping together) and the organic muds plot in the opposite direction to the PCBs.

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	0.775	71.3	71.3
2	7.39E-2	6.8	78.1
3	3.46E-2	3.2	81.3
4	3.18E-2	2.9	84.2
5	3E-2	2.8	87.0

Eigenvectors

(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
PCB 18	0.217	0.054	0.034	-0.251	-0.002
PCB 28	0.236	0.377	-0.650	0.037	0.022
PCB 52	0.231	-0.071	-0.026	-0.230	0.249
PCB 49	0.212	-0.167	0.054	-0.075	0.665
PCB 47	0.246	-0.113	-0.001	0.065	0.183
PCB 44	0.216	0.000	-0.075	-0.113	0.064
PCB 66	0.130	0.785	0.324	0.045	0.242
PCB 101	0.252	0.145	0.408	0.475	-0.151
PCB 151	0.259	-0.027	0.150	-0.239	-0.316
PCB 118	0.212	-0.033	-0.046	0.102	0.032
PCB 153	0.219	0.004	0.062	-0.190	-0.137
PCB 105	0.188	-0.148	0.249	-0.305	-0.108
PCB 141	0.169	0.016	-0.004	0.093	0.006
PCB 138	0.217	0.020	-0.169	0.056	-0.109
PCB 183	0.256	-0.061	-0.026	-0.100	-0.191
PCB 128	0.252	-0.126	-0.123	-0.045	0.073
PCB 156	0.279	-0.165	0.084	0.212	0.172
PCB 180	0.227	0.094	-0.140	-0.118	-0.277
PCB 170	0.202	-0.065	0.228	-0.017	-0.179
PCB 194	0.187	-0.100	-0.256	0.474	-0.155
LOI	-0.004	-0.053	-0.079	-0.030	0.157
TOC %	-0.006	-0.006	-0.021	0.025	0.050
% Sand	0.077	-0.259	0.089	0.335	0.048
% Mud	-0.025	0.087	-0.032	-0.120	-0.020

5.8.3 Upper Marsh Core PAH, Organic Matter and Grain Size PCA

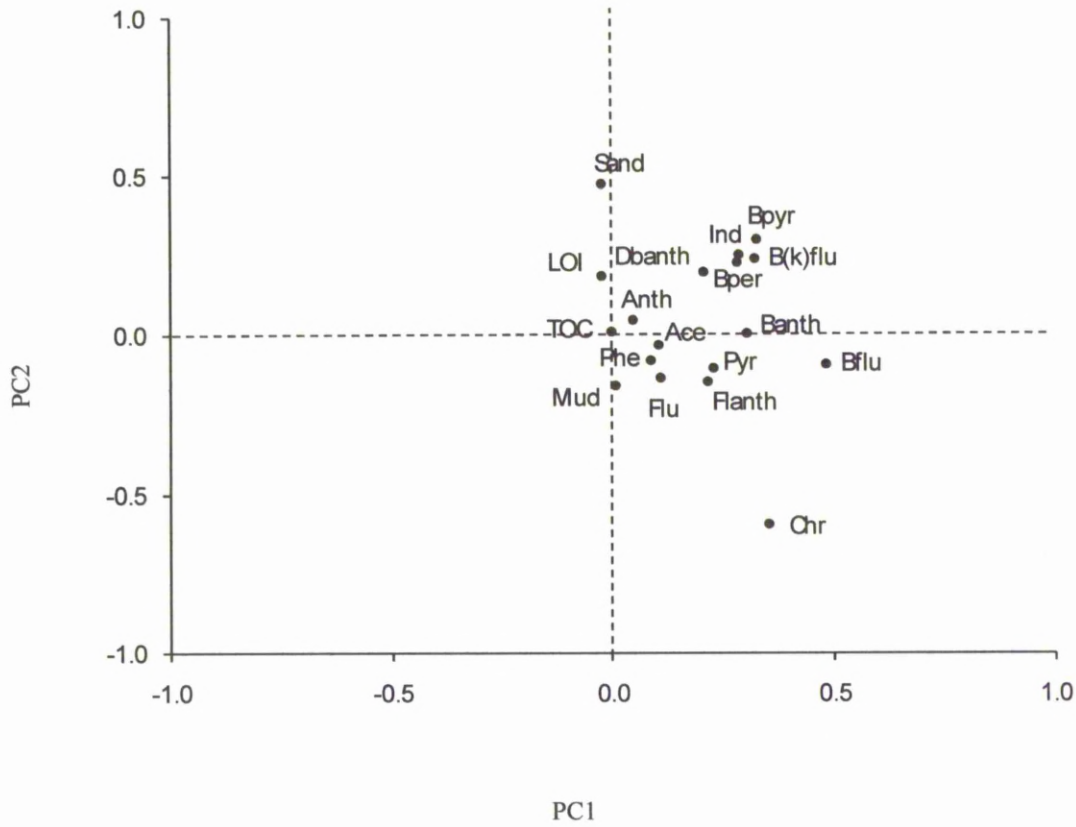


Figure 21: PCA scatter plot of Eigenvectors comparing PAHs, organic matter and grain size The relationship between PCA 1 (which explained 58.2% of the total variance) and PCA 2 (which explained a further 10.5%) is shown, along with graphical representations of the contributions of the original variables to both PC 1 and PC 2.

The first 3 components account for 78% of the variation in the data. There appear to be 2 main groups of PAHs with the lower molecular weight ones predominately in the top group and the higher molecular weight PAHs in the bottom group (there is some overlap between the groupings though).

		Eigenvalues	
PC	**Eigenvalues**	**%Variation**	**Cum.%Variation**
1	0.301	58.2	58.2
2	5.44E-2	10.5	68.7
3	4.87E-2	9.4	78.2
4	3.82E-2	7.4	85.6
5	2.23E-2	4.3	89.9

Eigenvectors

(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Acenaphthene (Ace)	0.104	-0.033	-0.245	0.059	-0.179
Fluorene (Flu)	0.111	-0.133	-0.231	0.135	-0.100
Phenanthrene (Phe)	0.090	-0.077	-0.304	0.006	-0.411
Anthracene (Anth)	0.046	0.047	-0.093	-0.038	-0.292
Fluoranthene (Flanth)	0.218	-0.146	-0.218	-0.480	-0.061
Pyrene (Pyr)	0.231	-0.102	-0.120	-0.465	0.087
Chrysene (Chr)	0.355	-0.593	-0.031	0.389	0.512
Benzo (a) anthracene (Banth)	0.307	0.003	0.091	-0.448	0.204
Benzo (b) fluoranthene (Bflu)	0.482	-0.094	0.721	0.051	-0.424
Benzo (k) fluoranthene (B(k)flu)	0.321	0.237	-0.192	-0.023	0.003
Benzo(a)pyrene (Bpyr)	0.328	0.298	-0.252	0.109	0.119
Indeno(1,2,3-cd)pyrene (Ind)	0.285	0.251	-0.085	0.182	0.021
Benzo (ghi) perylene (Bper)	0.280	0.226	-0.010	0.179	-0.004
Dibenz(a,h)anthracene (Dbanth)	0.206	0.195	-0.150	0.190	-0.022
LOI	-0.023	0.187	-0.027	0.227	-0.120
TOC %	-0.001	0.012	-0.010	0.004	0.009
% sand	-0.022	0.475	0.236	-0.098	0.400
% mud	0.006	-0.155	-0.086	0.029	-0.141

5.9 Chapter Summary

The main grain size is in the mud fraction with the dominant magnetic mineral being magnetite. Correlations and PCA suggest the behaviour of a number of minerals (Si, Al, Ca, Zr, Ti, Sr, Ni) is related to lithogenic factors, whilst grain size seems to have an influence on Si, Cl, Br, Al, Zr, Fe, Ca, K, S, Ni, Pb, Zn, Hg, Cd, Rb, Sr, PAHs, and PCBs. There also seems to be a diagenetic control on Fe, Mn, Br, Cl, Si, Pb, Zn, Cr. Pb, Zn, Cd, Hg, PCBs and PAHs would appear to be related to pollution input in the estuary.

The main pollutant metals show a general decrease in concentration towards the surface of the core, but this is not repeated for the PCBs and PAHs.

CHAPTER 6
OGLET BAY CHANNEL CORE RESULTS

The following chapter is a description of the results from the sediment core taken from the Channel core location on the Oglet Bay saltmarsh. It shows the downcore profiles of particle size, magnetic and metal distribution and also provides a description of the statistical analysis carried out on the data (Correlation coefficients and Principal Component Analysis).

6.1 Channel Core Particle Size Analysis

Particle size distribution data indicate the sediments are, for the most part, unimodal, poorly sorted and a mix of very fine sand and very coarse silt (Figure 22). Using the Folk and Ward (1957) description they are poorly sorted, finely skewed, mesokurtic coarse silt (Figure 23a-d). Mean grain size shows an overall increase down core with some variation in the degree of skewness, although never strongly skewed either way. The majority of the sediment is mud with around 20% sand (Figure 23e). The relative percentage of sand increases towards the bottom of the core, whilst the percentage of mud decreases sympathetically.

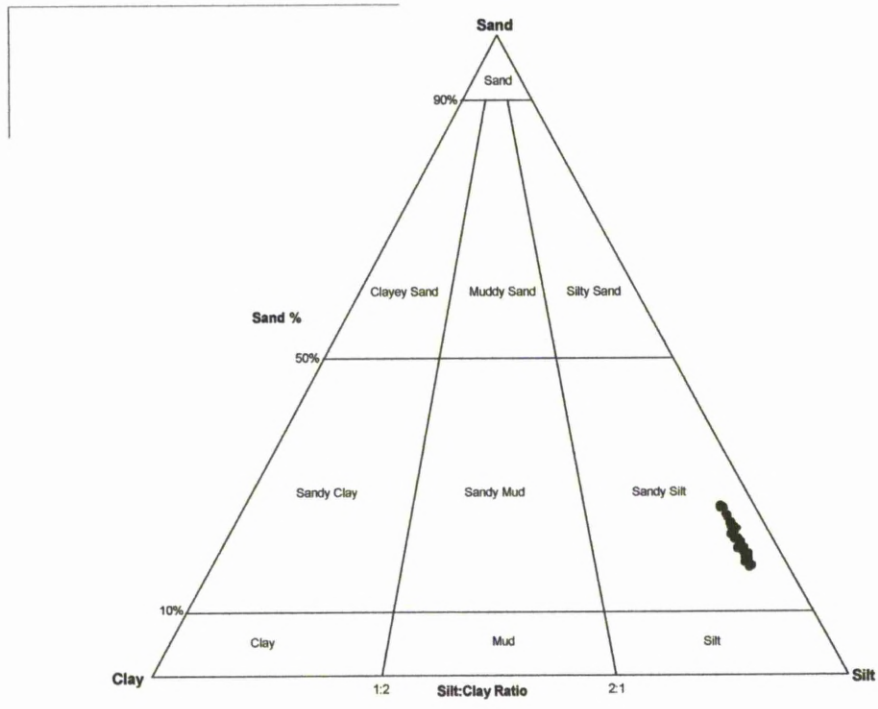


Figure 22: Channel core particle size distribution.

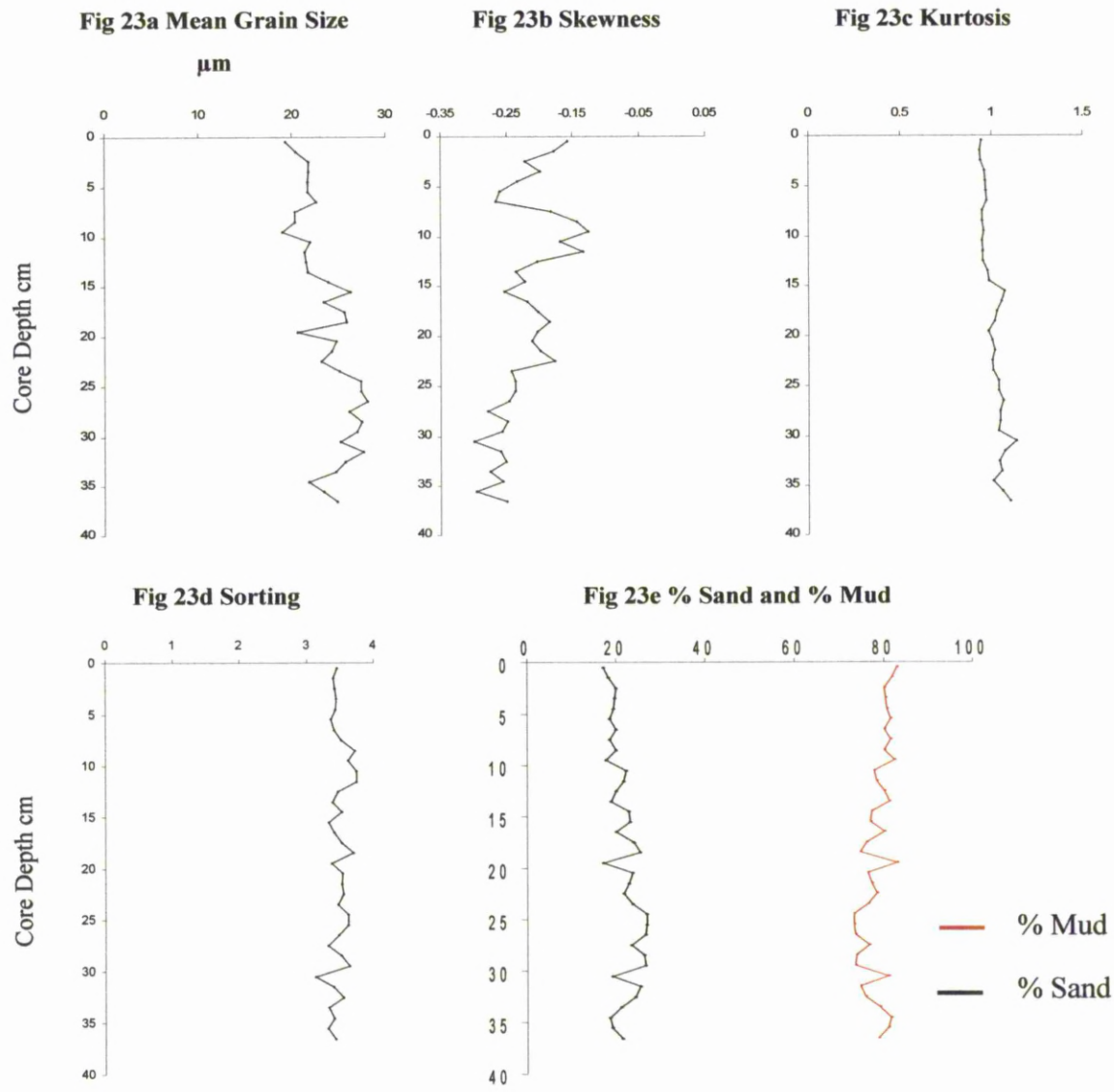


Figure 23a-e: Channel core particle size.

6.2 Channel Core Element Data

Si (Fig 24a) concentration show lower concentrations at 3cm, 6-12cm and again at 18-25cm. They are below ASV.

Al (Fig 23b), Ti (Fig 23c), K (Fig 24e), Sr (Fig 24s) and Fe (Fig 24g) values are below ASV and remain fairly constant downcore with only subtle variation.

Ca (Fig 23d) concentrations are above ASV and show a slight decrease downcore, but with more marked decreases at 3cm and 12cm.

S (Fig 24f) shows a slight decrease in the top 4cm of the core, followed by a marked increase in concentration with depth to 26cm, where levels decrease to 32cm and then show a slight increase at the very bottom of the core.

Mn (Fig 23h) values are slightly above ASV and fluctuate in the top part of the core. At 25cm they show a decrease and are below ASV at 27cm. At 30cm they show a return to values around ASV towards the bottom of the core.

Cl (Fig 24i) values increase in the first 2cm, then show a decrease to 5cm followed by an increasing concentration to 11cm. They then fluctuate considerably downcore with a high at 20cm, but the trend is an overall decrease. Concentrations are well above ASV.

Rb (Fig 24j) concentrations decrease to 5cm, at which point they show an increase to 14cm. Concentrations fluctuate considerably downcore and are below ASV.

After an initial increase in the top 5cm, Zr (Fig 24k) shows an overall decrease to 14cm followed by a slight downcore increase. Concentrations are well above ASV.

The concentrations of Y (Fig 24l) fluctuate wildly downcore but are above ASV.

Br (Fig 24m) values are well above ASV and show an overall decrease with depth. Two large fluctuations are increases at 10cm and 25cm and decreases at 5cm and 21cm. These trends are similar to those of LOI (Fig 24t) where the values are generally lower below 25cm. % LOI shows a slight overall downcore decrease. However, there is a larger decrease at 19cm and another at 27cm.

Cd (Fig 24n), Pb (Fig 24r) and Zn (Fig 24q) are all above ASV and show similar increases in concentration with depth, particularly at 10cm, 22cm and 35cm. Hg (Fig 18o) also increases with depth and is above ASV but fluctuates more in the top part of the core than Cd, Zn or Pb.

Ni (Fig 24p) values fluctuate considerably downcore but concentrations are generally below ASV.

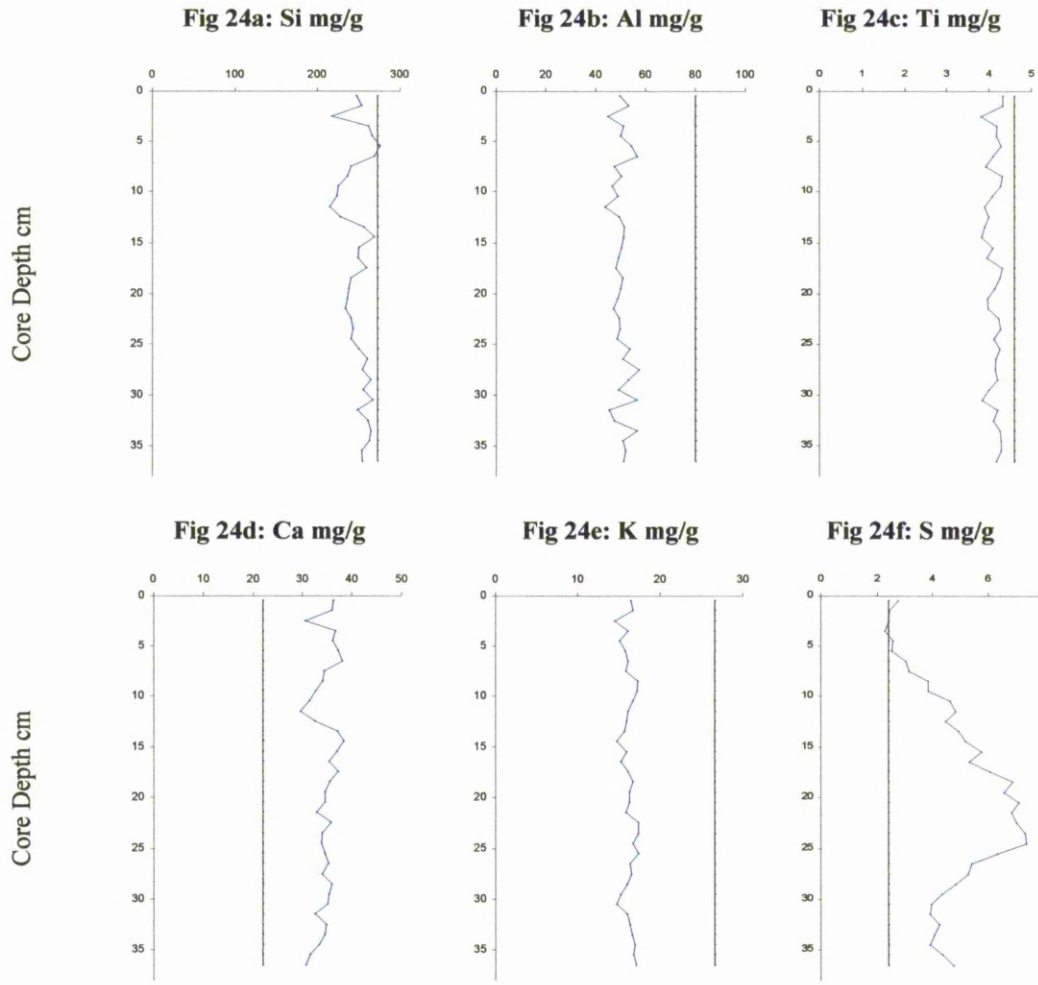


Fig 24g: Fe mg/g

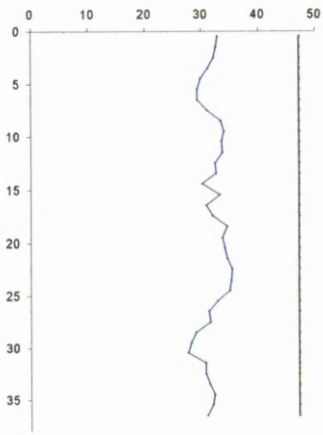


Fig 24h: Mn mg/g

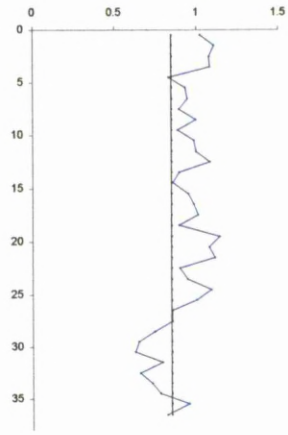
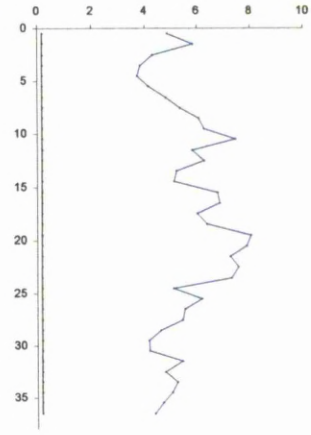


Fig 24i: Cl mg/g



Core Depth cm

Fig 24j: Rb µg/g

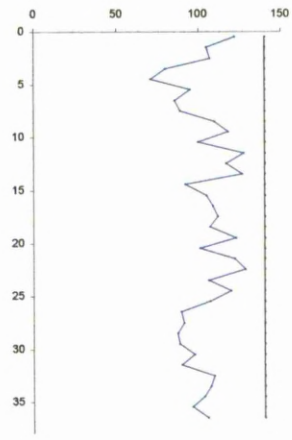


Fig 24k: Zr µg/g

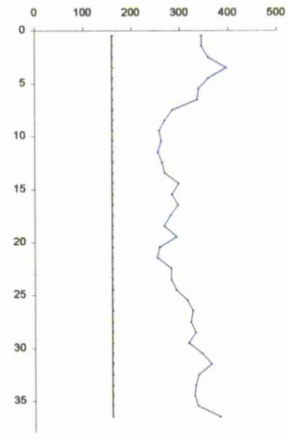
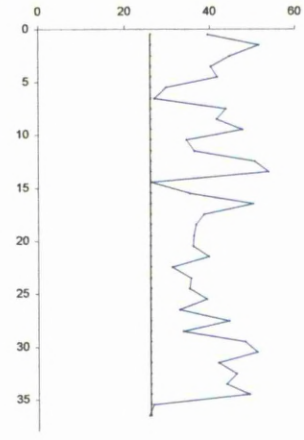


Fig 24l: Y µg/g



Core Depth cm

Fig 24s: Sr µg/g

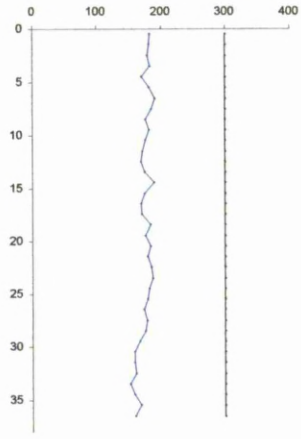
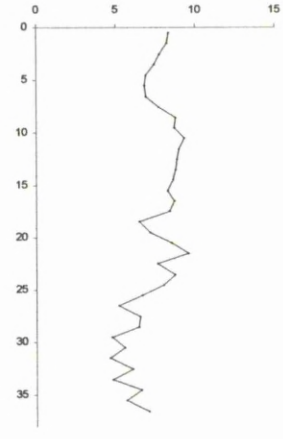


Fig 24t: LOI %



Core Depth cm

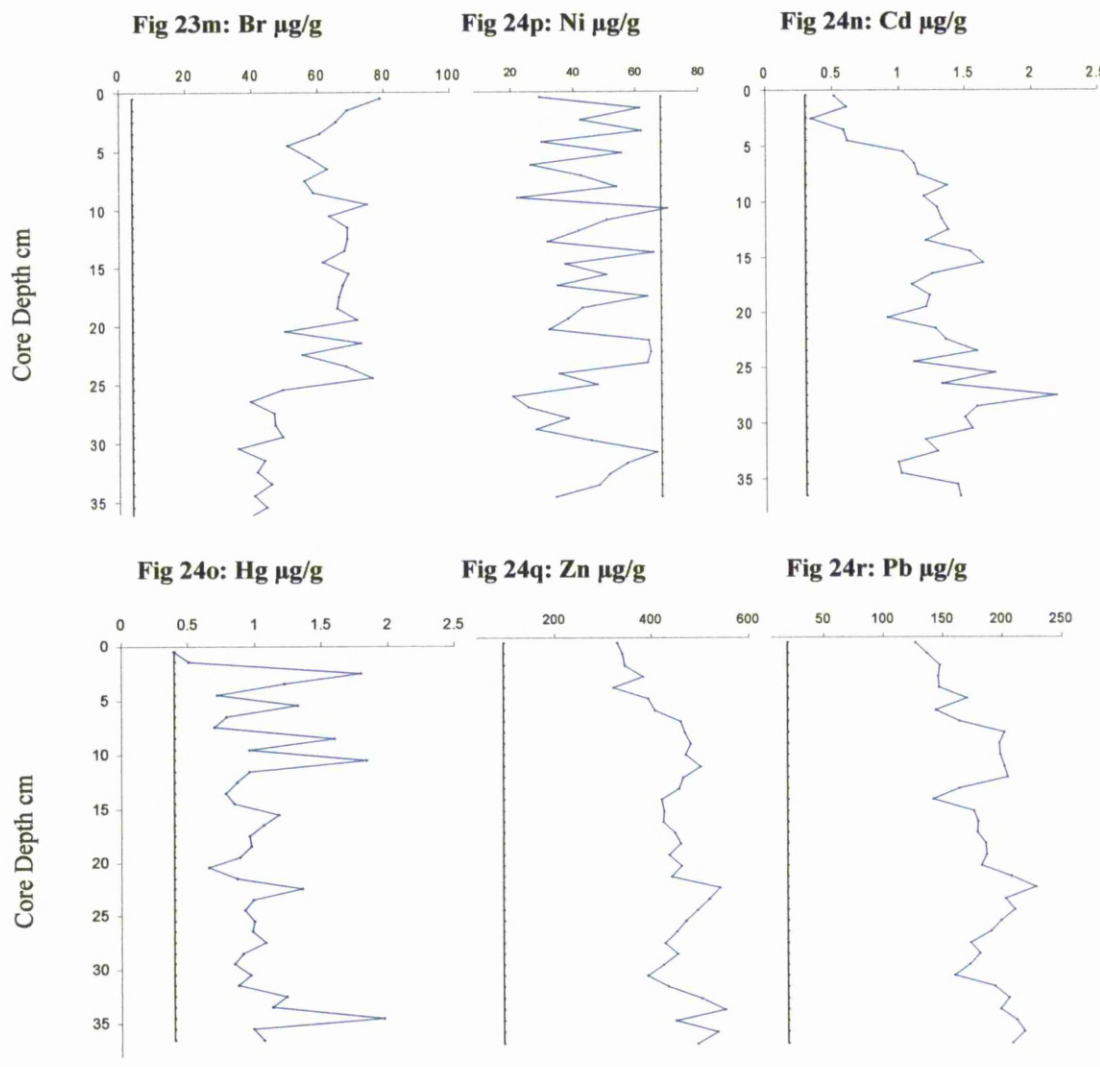


Figure 24a-r: Channel Core Element Concentrations (Average Shale Values (ASV) are shown in black for comparison with potential natural background concentrations, the data shown in blue are from the upper marsh sediments).

6.3 Channel Core Magnetics Data

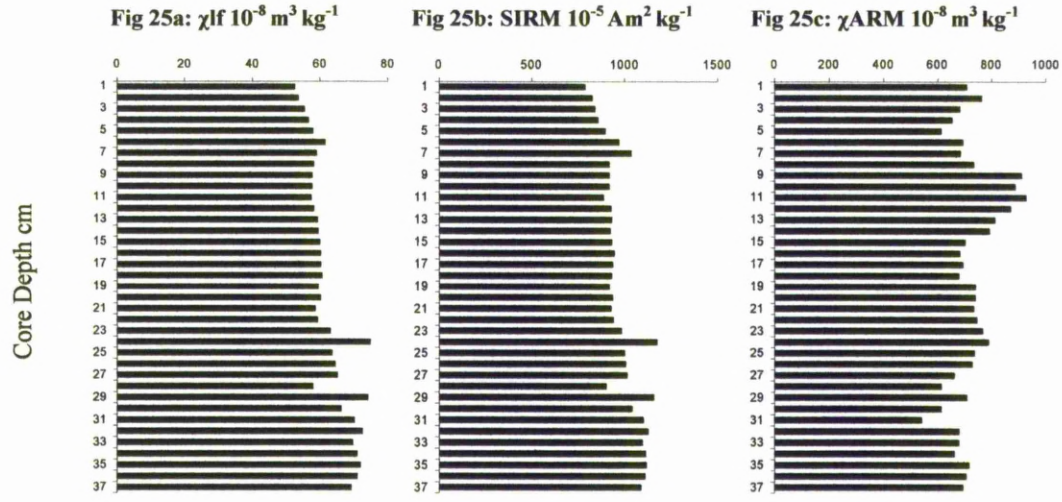
There is a slight overall downcore increase in χlf (Fig 25a), SIRM (Fig 25b) and Soft (Fig 25i) values. They show subtle peaks at 6cm, 24cm and 29cm depth.

χARM (Fig 25c), χARM/SIRM (Fig 25d) and χARM/χlf (Fig 25f), values decrease slightly downcore but there is a peak between 9cm and 12cm. This is likely to be due to the influence of grain size, the higher values indicating the presence of finer grains.

SIRM/χlf (Fig 25e) values are fairly consistent with depth but there is a slight peak at 7cm. HIRM (Fig 19g) and Hard % (Fig 19h) values are fairly constant with depth but both show a large peak at 7cm.

FD% (Fig 25j) values increase in the top part of the core and then fluctuate around 2% down to 20cm where there is a peak followed by a considerable drop in the values. There is another large drop at 31cm.

-20mT values fluctuate slightly downcore with a peak at 7cm and a drop at 25cm. -300mT IRM reverse values are constant with depth except for a drop at 7cm (Fig 25k). There is no evidence of significant backfield divergence down-core.



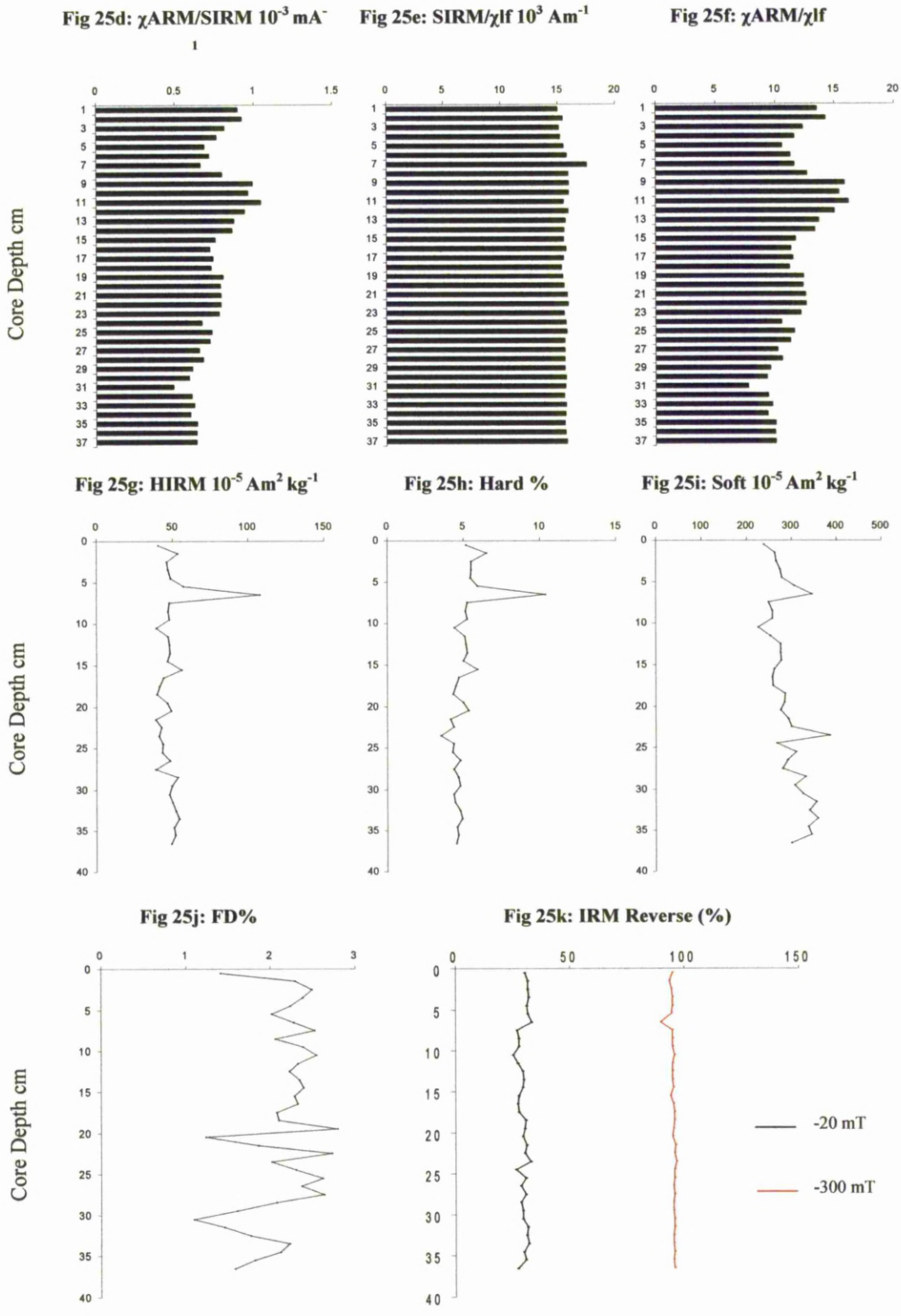


Figure 25a-k: Channel Core Magnetics Data.

6.4 Channel Core Correlations

Positive and negative correlations were considered at both 0.01 and 0.05 levels of significance. SPSS highlighted both strong correlations and those with a weaker but significant link. Correlations were taken to be strongly significant if they were over 0.7, i.e. 49% or more of the variance could be explained by the correlation. However, weaker correlations (under 0.7) that have been highlighted by SPSS as showing a significant relationship within the data have also been discussed.

6.4.1 Channel Core Element Correlations (See appendix 1)

Si shows a weak positive correlation at the 0.01 significance levels with the Al, Ca, Zr, % very coarse silt, SIRM/ARM and Soft and a weak negative correlation with Fe, Mn, Cl, Br, Rb, LOI, Sorting, Skewness, % medium silt, % fine silt, % very fine silt, χARM, χARM/SIRM, χARM/χlf, ARM. At the 0.05 significance level Si shows a weak positive correlation with χlf, SIRM, -20mT and HIRM and a weak negative one with Pb and % clay.

Al shows a weak positive correlation at the 0.01 level with Si, Ca, SIRM/ARM and % very coarse silt and a weak negative correlation with χARM, ARM, Sorting and skewness. It also shows a weak positive correlation at the 0.05 level of significance with Zr, HIRM, Soft and -20mT and a weak negative one with Fe, Br, LOI, % very fine silt, χARM/SIRM and χARM/χlf.

Ti shows a strong positive correlation with K at the 0.01 significance level.

Ca shows a weak positive correlation with Si and Al and a weak negative correlation with Pb at the 0.01 significance level. At the 0.05 significance level it shows a weak positive correlation with Sr and Hard % and a weak negative one with Zn, Hg, χARM, ARM and -300mT.

K shows a weak positive correlation at the 0.01 level with Fe, Pb, Zn, χARM and ARM and a strong positive correlation with Ti. At the lower 0.05 significance level it shows a weak positive correlation with Cl and sorting.

Fe shows a weak positive correlation at the 0.01 level with K, Mn, S, Pb, Br, Rb, LOI, Sorting, Skewness, χARM, χARM/SIRM, χARM/χlf and ARM, a strong positive correlation with Cl and a weak negative one with Si, Zr, % very coarse silt and SIRM/ARM. At the 0.05 significance level it shows a weak positive correlation with Zn, and % fine sand and weak negative one withAl and HIRM.

Mn shows a weak positive correlation (at the 0.01 level) with Fe, Cl, Sr, LOI, χARM, χARM/SIRM, χARM/χlf, ARM, skewness, % medium silt and % fine silt and a strong positive one with Br. It also shows a weak negative correlation with Si, χlf, SIRM, Soft, % medium sand and % very coarse silt and a strong one with Cr and SIRM/ARM. At the 0.05 level of significance it shows a weak positive correlation with Rb, Cd, % very fine silt and % FD and a weak negative one with mean grain size.

S shows a weak positive correlation, at the 0.01 level, with Fe, Cl, Pb, Zn, Rb, Cd, mean grain size, % sand and -300mT, a strong one with % fine sand and a weak negative one with Zr, Hard %, % mud, % fine silt, % very fine silt and % clay. It also shows a weak positive correlation at the 0.05 level with kurtosis and a weak negative one with % medium silt and HIRM.

At the 0.01 significance level Cl shows a weak positive correlation with Mn, S, Pb, Rb, LOI and skewness, % fine sand, χARM, χARM/SIRM, χARM/χlf and ARM, a strong positive one with Fe, a weak negative correlation with Si and SIRM/ARM and a strong negative one with Zr. At the lower level of significance (0.05) it shows a weak positive correlation with K, Zn and Br and a weak negative one with % coarse silt.

Pb shows a weak positive correlation at the 0.01 level with K, Fe, S, Cl, Cd, % fine sand, χlf, SIRM and -300mT, a strong positive one with Zn and a weak negative correlation with Ca, and Hard %. At the 0.05 level of significance it shows a weak positive correlation with Rb, Hg, kurtosis, χARM and ARM and a weak negative one with Si, Zr and Sr.

Zn shows a strong positive correlation at the 0.01 level with Pb, and weak positive correlations with K, S, Cd, % fine sand, χlf and SIRM. It shows a weak negative correlation with Zr. At the 0.05 level of significance it shows a weak positive correlation with Fe, Cl, Rb, χARM, ARM, Soft and -300mT and a weak negative one with Ca and Hard %.

Br shows a weak positive correlation at the 0.01 level with Fe, Rb, Sr, χlf, χARM, χARM/SIRM, χARM/χlf, ARM, % medium silt, % fine silt and % very fine silt. It shows strong positive correlations with Mn and LOI. Br exhibits weak negative correlations with Si, Zr, Cr, SIRM, Soft, mean grain size, kurtosis, % medium sand, % very coarse silt, and a strong negative correlation with SIRM/ARM. At the 0.05 level of significance it shows a weak positive correlation with Cl and FD% and a weak negative one with Al and % coarse sand.

Zr shows a weak positive correlation at the 0.01 level with Si, LOI, SIRM/ARM, -20mT and % very coarse silt, a weak negative one with Fe, S, Zn, Br, Rb, χARM, χARM/SIRM, χARM/χlf, ARM, sorting, skewness and % fine sand and a strong negative one with Cl. At the 0.05 level it shows a weak positive correlation with Al and Soft and a weak negative one with Pb.

Rb shows a weak positive correlation at the 0.01 level with Fe, S, Cl, Br, χARM, χARM/SIRM, χARM/χlf and ARM and a weak negative correlation with Si, Zr and SIRM/ARM. At the 0.05 level it shows a weak positive correlation with Mn, Pb and Zn and a weak negative one with Al, % very fine sand and % very coarse silt.

Sr shows a weak positive correlation with Mn, Br, LOI, χlf, χARM/SIRM and χARM/χlf and it has weak negative correlations with Kurtosis, % very coarse silt, SIRM and SIRM/ARM at the 0.01 level. It shows a weak positive correlation with Ca, Fe, Skewness, % medium silt, % fine silt, % very fine silt and FD% and a weak negative one with Pb, Cr, Y, % coarse sand and soft at the 0.05 level of significance.

Cr shows a weak positive correlation at the 0.01 level with Kurtosis, χlf, SIRM, SIRM/ARM and soft, a strong positive one with Mn and a weak negative one with Br, LOI, % medium silt, χARM/SIRM and χARM/χlf. At the 0.05 level of

significance it shows a weak positive correlation with Cd, Mean grain size, % very coarse silt, and -300mT and a weak negative one with Sr, Skewness, % fine silt, % very fine silt and Hard %.

Ni has a weak positive correlation at the 0.05 level with Hg.

Y is has a weak negative correlation with Sr at the 0.05 level.

LOI shows a weak positive correlation at the 0.01 level with Fe, Mn, Cl, Rb, Sr, Mean grain size, Skewness, % medium silt, % fine silt, % very fine silt, % clay, χARM and ARM, a strong positive correlation with Br, χARM/SIRM and χARM/χlf, a weak negative one with Si, Zr, Cr, kurtosis, % medium sand, % very coarse silt, χlf, SIRM and Soft and a strong negative correlation with SIRM/ARM. It shows a weak positive correlation with sorting and a weak negative one with Al and -20mT at the 0.05 level.

Cd shows weak positive correlations at the 0.01 significance level with S, Pb, Zn, mean grain size, kurtosis, % sand, % fine sand and SIRM and a weak negative correlation with % mud, % medium silt, % fine silt and % very fine silt. At the lower 0.05 level of significance it shows a weak positive correlation with Cr, % very coarse silt and χlf and a weak negative one with Mn and % clay.

Hg shows a weak positive correlation with Pb and Ni and a weak negative one with Ca at the 0.05 level.

6.4.2 Channel Core Magnetic Correlations (See appendix 1)

χlf shows a weak positive correlation with mean grain size, kurtosis, % medium sand and % very coarse silt, a strong positive one with SIRM, SIRM/ARM and Soft, a weak negative one with Skewness, % fine silt, % very fine silt, % clay and ARM and a strong negative correlation with % medium silt, χARM/SIRM and χARM/χlf at the 0.01 level. It shows a weak positive correlation with % sand and -300Mt and weak negative one with % mud, FD% and Hard % at the 0.05 level.

%FD shows a weak negative correlation with SIRM/ARM at the 0.01 level of significance. At the 0.05 level of significance it shows a weak positive correlation with χARM/SIRM and χARM/χlf and a weak negative one with Kurtosis, % medium sand, % very coarse sand, χlf and SIRM.

SIRM shows a weak positive correlation with Mean Grain Size, kurtosis, % medium sand and % very coarse silt, a strong positive correlation with χlf, SIRM/ARM and Soft, a weak negative one with Skewness, % medium silt, % fine silt, % very fine silt and a strong negative correlation with χARM/SIRM and χARM/χlf at the 0.01 significance level. At the 0.05 significance level it shows a weak positive correlation with % sand and a weak negative one with % mud, % clay and FD%.

At the 0.01 level of significance χARM shows a weak positive correlation with Sorting, % medium silt, % fine silt, % very fine silt and % clay and a strong positive correlation with Skewness, χARM/SIRM, χARM/χlf and ARM. It has a weak negative correlation with Mean grain size and SIRM and strong negative one with % very coarse silt and SIRM/ARM. It shows a weak negative correlation with % very fine sand, Soft and -20mT at the 0.05 Level.

χARM/SIRM shows a weak positive correlation with % clay and Sorting, a strong positive one with Skewness, % medium silt, % fine silt, % very fine silt, χARM, χARM/χlf and ARM, a weak negative correlation with mean and % very fine sand, and a strongly negative one with Kurtosis, % very coarse silt, χlf, SIRM, SIRM/ARM and soft at the 0.01 level. It is shows a weak positive correlation with % mud and FD% and a weak negative one with -20mT, % medium sand and % sand at the 0.05 level.

SIRM/χlf shows a weak positive correlation with Hard % and a strong positive one with HIRM at the 0.01 level. At the 0.05 level it shows a weak negative one with -300mT.

χARM/χlf shows a weak positive correlation with Sorting, a strong positive correlation with skewness, % medium silt, % fine silt, % very fine silt, % clay, χARM, χARM/SIRM and ARM, a weak negative correlation with mean grain size,

% very medium sand and % very fine sand and a strong negative correlation with kurtosis, % very coarse silt, χlf, SIRM, SIRM/ARM and Soft at the 0.01 level of significance. At the 0.05 level it shows a weak positive correlation with % mud and FD% and a weak negative one with % sand and -20mT.

HIRM shows a strong positive correlation with Hard % and SIRM/χlf and a strong negative one with -300mT at the 0.01 level. At the 0.05 level it shows a weak positive correlation with Soft and -20mT and a weak negative one with % fine sand.

At the 0.01 level Hard % shows a weak positive correlation with SIRM/χlf, a strong positive one with HIRM, a weak negative one with % fine sand and a strong negative one with -300mT. At the 0.05 level it shows a weak positive correlation with % mud % and a weak negative one with mean grain size, kurtosis, % sand and χlf.

ARM shows a weak positive correlation with Sorting, % medium silt, % fine silt, % very fine silt and % clay, a strong positive one with skewness, χARM, χARM/SIRM, χARM/χlf, a weak negative correlation with mean grain size and kurtosis and a strong negative one with % very coarse silt and SIRM/ARM at the 0.01 level. It shows a weak negative correlation with % very fine sand, soft and -20mT at the 0.05 level.

SIRM/ARM shows a weak positive correlation with mean grain size, a strong positive one with kurtosis, % very coarse silt, χlf, SIRM and Soft, a weak negative one with sorting, % clay and FD% and a strong negative correlation with Skewness, % medium silt, % fine silt, % very fine silt, χARM, χARM/SIRM and χARM/χlf at the 0.01 level. It shows a weak positive correlation with % very fine sand at the 0.05 level.

At the 0.01 level of significance Soft shows a weak positive correlation with Mean grain size, kurtosis, % very coarse silt and -20mT and a strong positive one with χlf, SIRM and SIRM/ARM. It shows a weak negative correlation with Skewness, % medium silt, % fine silt, % very fine silt and % clay and a strong negative one with χARM/SIRM and χARM/χlf. At the 0.05 level it shows a weak positive correlation

with % very fine sand and HIRM and a weak negative one with Sorting, χARM and ARM.

-20mT exhibits a weak positive correlation with Soft, and a weak negative one with Sorting at the 0.01 level. At the 0.05 level it shows a weak positive correlation with HIRM and a weak negative one with Skewness, % fine sand, χARM, χARM/SIRM, χARM/χlf and ARM.

-300mT shows a weak positive correlation with % fine sand, a weak negative one with SIRM/χlf and a strong negative correlation with HIRM and Hard % at the 0.01 level. It shows a weak positive correlation with Mean grain size, % sand and χlf and a weak negative one with % mud at the 0.05 level.

Again, despite the highly dynamic tidal channel setting of this core, these correlations suggest a clear grain-size influence on the magnetic properties of the sediment record (as will be discussed in the interpretations section).

6.5 Principal Component Analysis Channel Core

Multivariate statistical analysis using Principal Component Analysis (PCA) was undertaken in an attempt to establish relationships between organic matter, grain size and elements. The results of this are given below as a series of bivariate plots and associated eigenvectors and eigenvalues.

6.5.1 Channel Core Element, Organic Matter and Grain Size PCA

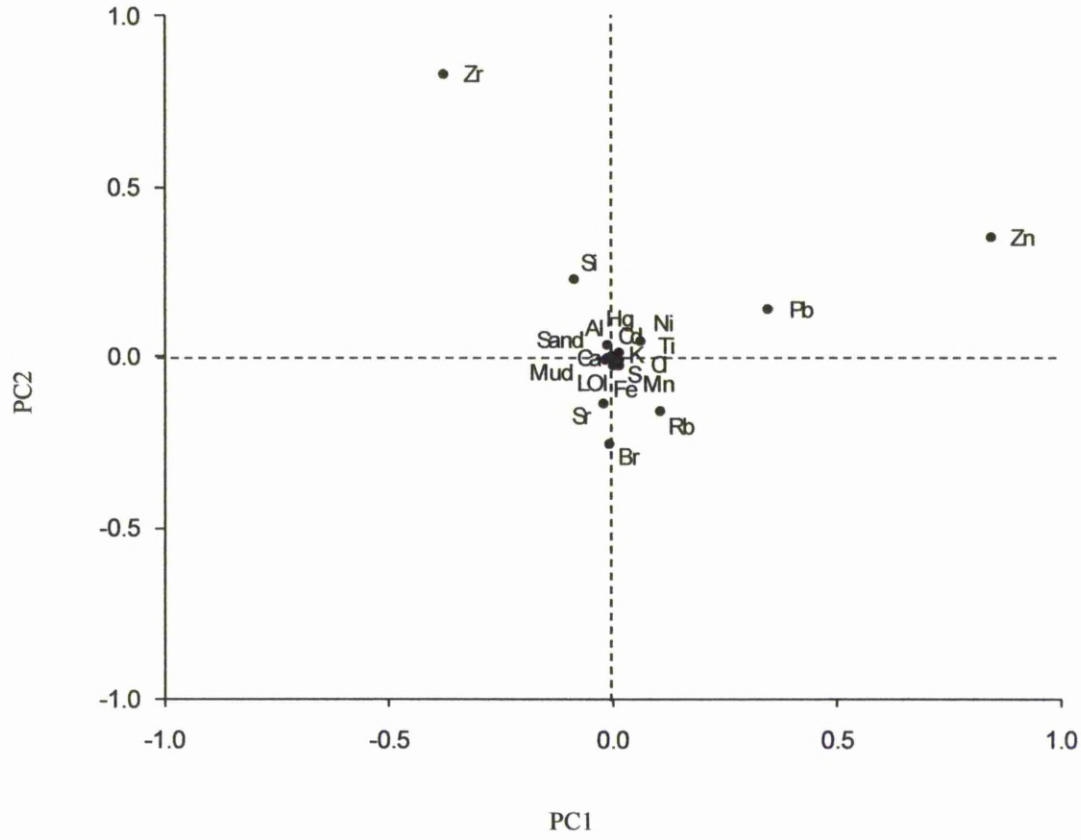


Figure 26: PCA Scatter plot of Eigenvectors comparing elements, organic matter and grain size. The relationship between PCA 1 (which explained 66.4% of the total variance) and PCA 2 (which explained a further 21.1%) is shown, along with graphical representations of the contributions of the original variables to both PC 1 and PC 2.

There appears to be 2 main groupings in the behaviour of the metals. Zr, Si and Al stand out as one group and could be related to lithogenic inputs. Zn, Pb Ni (and to a lesser degree Hg and Cd) would appear to suggest an input of pollution that is not related to grain size or mineral vs. organic content. A third grouping (Rb, Sr, Br) appears to illustrate a loose association between grain size (i.e. fine grain size) and organic matter.

		Eigenvalues	
PC	**Eigenvalues**	**%Variation**	**Cum.%Variation**
1	4.13E3	66.4	66.4
2	1.31E3	21.1	87.5
3	234	3.8	91.3
4	207	3.3	94.6
5	137	2.2	96.8

The first 3 components account for 91% of the variation in the data

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Si	-0.087	0.233	-0.589	0.031	0.066
Al	-0.010	0.032	-0.109	-0.014	-0.033
Ti	0.000	0.001	0.001	0.001	0.000
Ca	-0.013	-0.005	-0.090	0.036	-0.014
K	0.007	0.003	0.009	0.004	-0.005
Fe	0.016	-0.025	0.054	0.030	-0.015
Mn	0.000	-0.002	0.004	0.002	-0.002
S	0.015	-0.010	-0.006	-0.005	0.009
Cl	0.010	-0.018	0.009	0.004	0.011
Pb	0.348	0.138	0.477	-0.307	0.531
Zn	0.843	0.351	-0.198	0.106	-0.297
Br	-0.006	-0.259	0.192	0.267	-0.357
Zr	-0.377	0.828	0.296	0.082	-0.239
Rb	0.109	-0.163	0.444	0.010	-0.486
Sr	-0.018	-0.140	-0.118	0.262	-0.153
Ni	0.065	0.046	0.158	0.863	0.410
Hg	0.001	0.002	0.007	0.003	0.011
Cd	0.003	0.001	-0.008	-0.008	0.004
LOI %	0.002	-0.028	0.015	0.018	-0.017
% Sand	0.014	0.011	-0.036	-0.004	0.076
% Mud	-0.014	-0.011	0.036	0.004	-0.076

6.6 Chapter Summary

Due to the dynamic nature of the environment in which this core was collected it is likely that the strength of many of the relationships within the data has been weakened due to physical mixing. This could explain why many of the correlations calculated for this core fall below the selected 0.7 threshold. There are several that are over 0.6, which could indicate a relationship of some importance within the data.

The dominant magnetic mineral is magnetite. There is an increase in mean grain size downcore and a decrease in the amount of organic matter present. Even with the low correlations, it is still possible to identify correlations linked to lithogenic controls (Al, Si, Ca, Zr), sediment grain size (Ca, Zr, Si, Ti, K, Fe, S, Rb, Pb, Zn, Cd), organic matter (Mn, Br, Cl, Fe, Rb) and diagenetic behaviour (Fe, Mn and S) (see interpretations section). Pollution metals (Cd, Hg, Pb and Zn) show increasing concentrations downcore.

CHAPTER 7
SPEKE HALL LAKE RESULTS

The following chapter is a description of the results from the sediment core taken from the lake at Speke Hall. It shows the downcore profiles of particle size, magnetic, metal, PCB and PAH distribution and also provides a description of the statistical analysis carried out on the data (correlation coefficients and Principal Component Analysis and comparison of the treated and untreated data).

7.1 Speke Hall Lake Particle Size Analysis

Particle size distribution data indicate the sediments are unimodal, poorly sorted, very coarse fine silty sand. Using the Folk and Ward (1957) description they are poorly sorted, negatively skewed, leptokurtic with a mix of fine sand and very fine sand (fig 28b-c). Mean grain size (fig 28a) shows an overall decrease down core with some variation in the degree of skewness. The majority of the sediment is sand (Fig 20), with some mud. The relative percentage of sand decreases towards the bottom of the core while the percentage of mud increases (fig 28e).

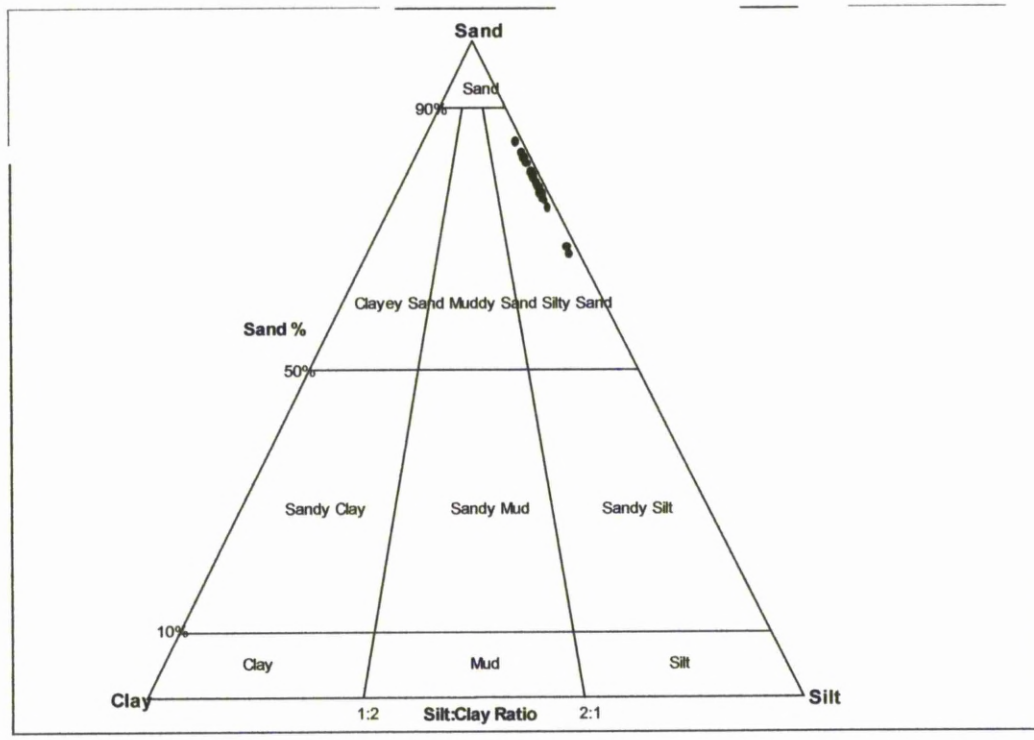


Figure 27: Speke Hall Lake Particle Size Distribution.

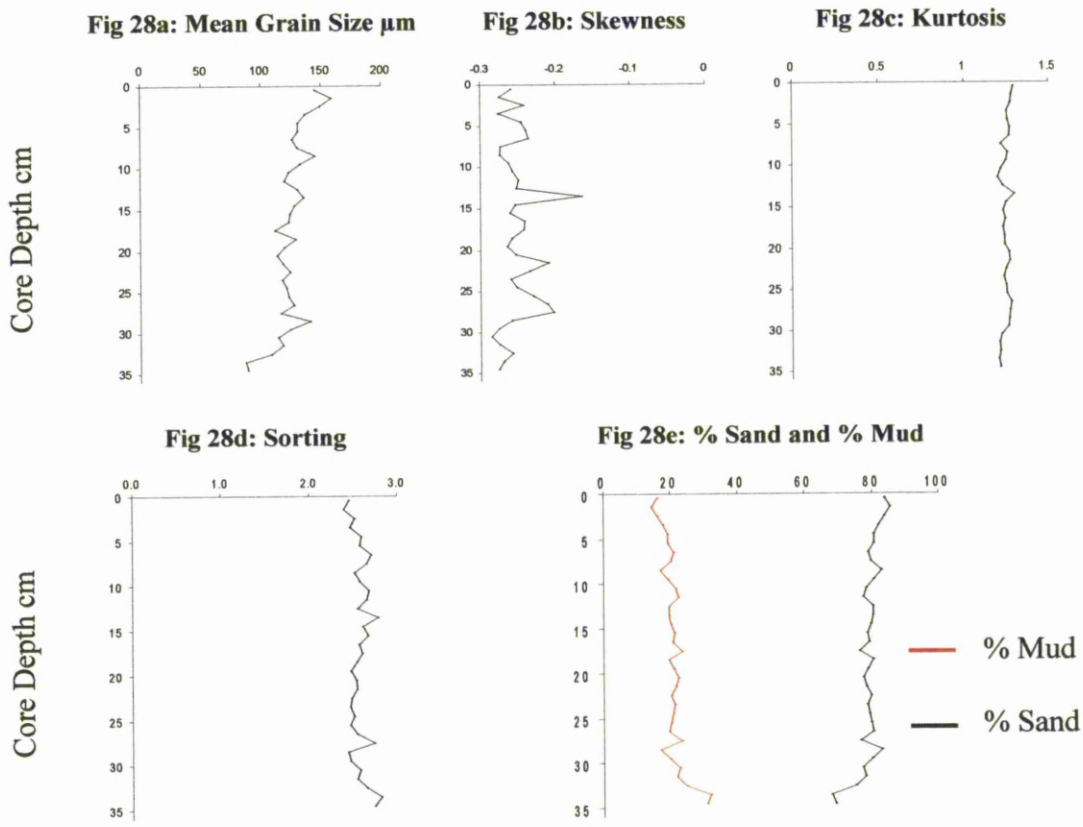


Figure 28a-e: Speke Hall Lake Particle Size.

7.2 Speke Hall Lake Sediment Element Data

Si (Fig 29a) shows a gradual downcore increase from 95mg/g at the surface to 129mg/g at the bottom of the core and all values are well below the ASV. Both treated and untreated sediment exhibit similar trends.

Al (Fig 29b) values gradually increase towards the bottom of the core. The untreated sediment concentrations are lower than the treated sediment concentrations but are within analytical uncertainty.

Ti (Fig 29c) and K (Fig 29e) show a steady downcore value with very little fluctuation in concentrations, and are well below ASV.

Ca (Fig 29d) shows a slight decrease in concentration form the top of the core to around 18cm depth, at which point its concentration increases towards the bottom of

the core, to around 27cm where it decreases again to 30cm and then starts to increase again. The concentrations are above ASV throughout the core.

The concentration of S (Fig 29f) is also well above ASV and decreases to around the 17cm mark, before it then starts to increase towards the bottom of the core. The untreated sediment concentrations are marginally lower than the treated sediment concentrations.

Fe (Fig 29g) sediment concentrations show a very slight overall increase downcore. The untreated sediment concentrations are lower than the treated sediment concentrations and values are well below ASV.

Mn (Fig 29h) values remain fairly constant down to 23-24cm after which they increase to the bottom of the core. The untreated sediment concentrations are lower than the treated sediment concentrations. Values are well below ASV.

P (Fig 29l) concentration is well above ASV and exhibits a downcore decrease to 9cm, it then remains constant to 28cm where it starts to increase in concentration again. The untreated sediment concentrations are lower than the treated sediment concentrations.

Ba (Fig 29j) values show a slight increase downcore. They are well below ASV.

Br (Fig 29k) fluctuates downcore and is well above ASV. The untreated sediment concentrations are lower than the treated sediment concentrations.

Mg (Fig 29i) values are fairly constant downcore and well below ASV.

As (Fig 29m), Cd (Fig 29n), Zn (Fig 29q), Pb (Fig 29r) and Ni (Fig 29p) values increase downcore. As, Cd, Pb and Zn are all well above ASV. Ni values are below ASV down to 25cm where they increase to over ASV. The Zn concentrations in the untreated sediment are lower than the treated sediment concentrations.

Hg (Fig 29o) concentrations are above ASV and fluctuate downcore. There appears to be a slight overall downcore increase with this trend being more obvious in the treated sediment samples.

Cr (Fig 29s) concentrations are below ASV and remain relatively constant downcore.

Cu (Fig 29t) concentrations are above ASV and exhibit a slight down core increase. The treated sediment show periodic high concentrations of Cu, suggesting that the ultrasonic extraction process may have enhanced the Cu in some sediments, whilst the untreated sediment shows a fairly stable down core increase.

Y (Fig 29y) increases downcore and concentrations are below ASV.

Rb (Fig 29v) and Sr (Fig 29w) values are below ASV and fairly constant downcore. Rb shows a slight increase towards the centre of the core and Sr increases slightly towards the bottom of the core.

Zr (Fig 29u) values show a downcore increase to around 25-26cm, followed by a decrease.

V (Fig 29x) shows a downcore increase and is below ASV. However, towards the bottom of the core the values are approaching ASV.

LOI (Fig 29z) shows a decrease downcore.

The metals Ca, S, Br, P, As, Cd, Hg, Ni (towards the bottom of the core), Zn, Pb and Cu are all found at concentrations above ASV. Of these the higher concentrations of As, Cd, Hg, Ni, Zn, Pb and Cu are almost definitely due to pollution inputs. High levels of S and Br can also be a result of a pollutant input, or can be due to natural processes.

Fig 29a: Si mg/g

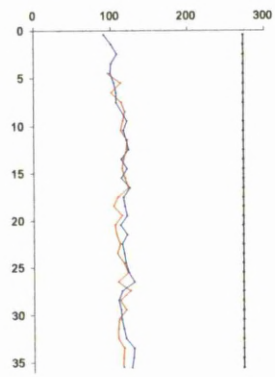


Fig 29b: Al mg/g

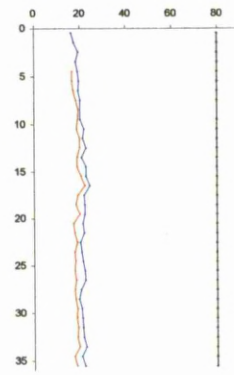
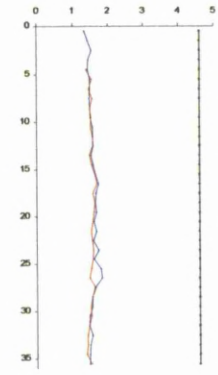


Fig 29c: Ti mg/g



Core Depth cm

Fig 29d: Ca mg/g

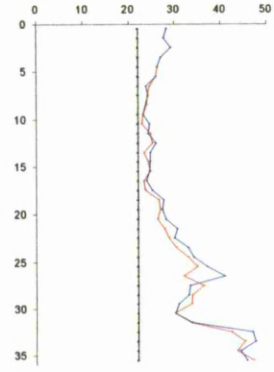


Fig 29e: K mg/g

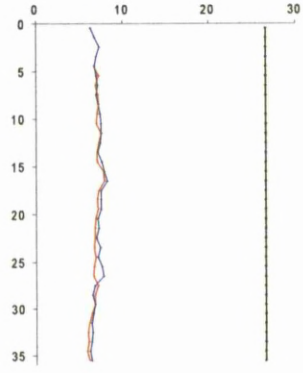
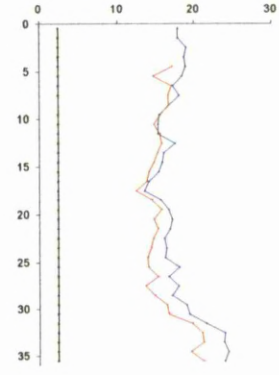


Fig 29f: S mg/g



Core Depth cm

Fig 29g: Fe mg/g

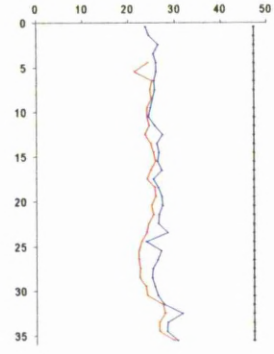


Fig 29h: Mn mg/g

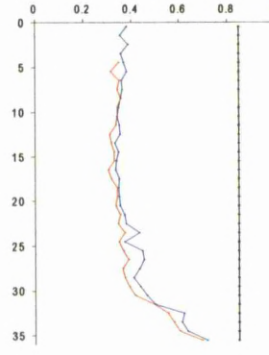
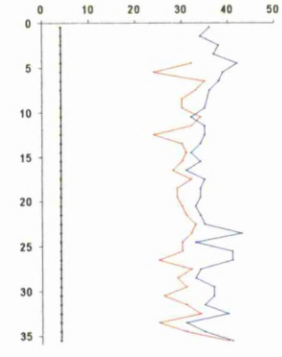


Fig 29k: Br µg/g



Core Depth cm

Fig 29i: Mg mg/g

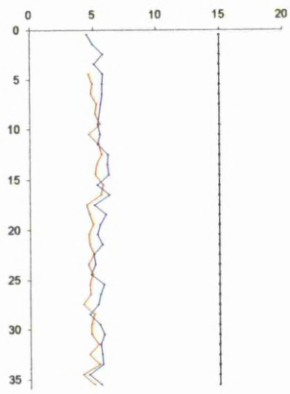


Fig 29j: Ba µg/g

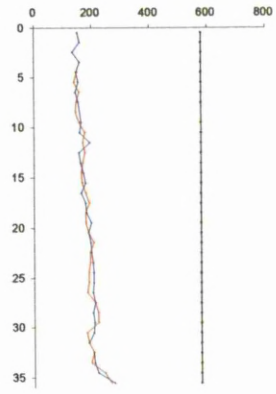
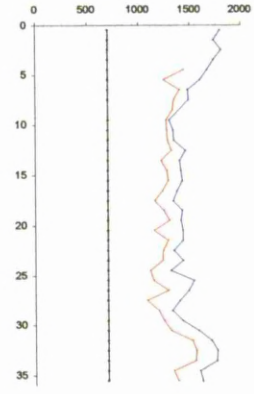


Fig 29l: P µg/g



Core Depth cm

Fig 29m: As µg/g

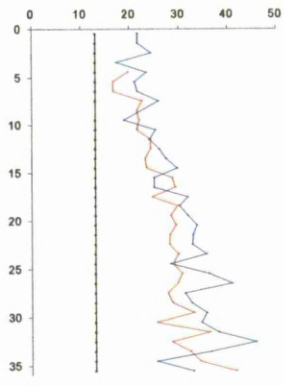


Fig 29n: Cd µg/g

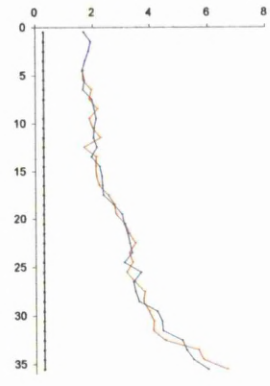
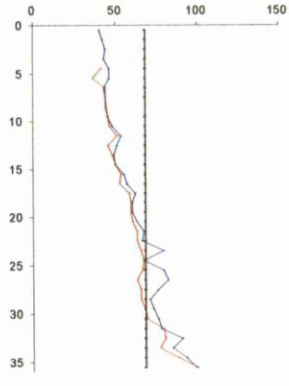


Fig 29p: Ni µg/g



Core Depth cm

Fig 29o: Hg µg/g

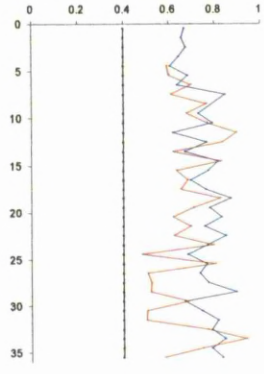


Fig 29q: Zn µg/g

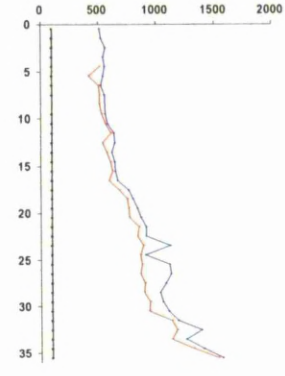
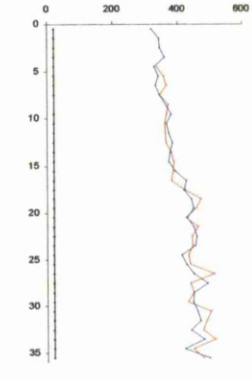


Fig 29r: Pb µg/g



Core Depth cm

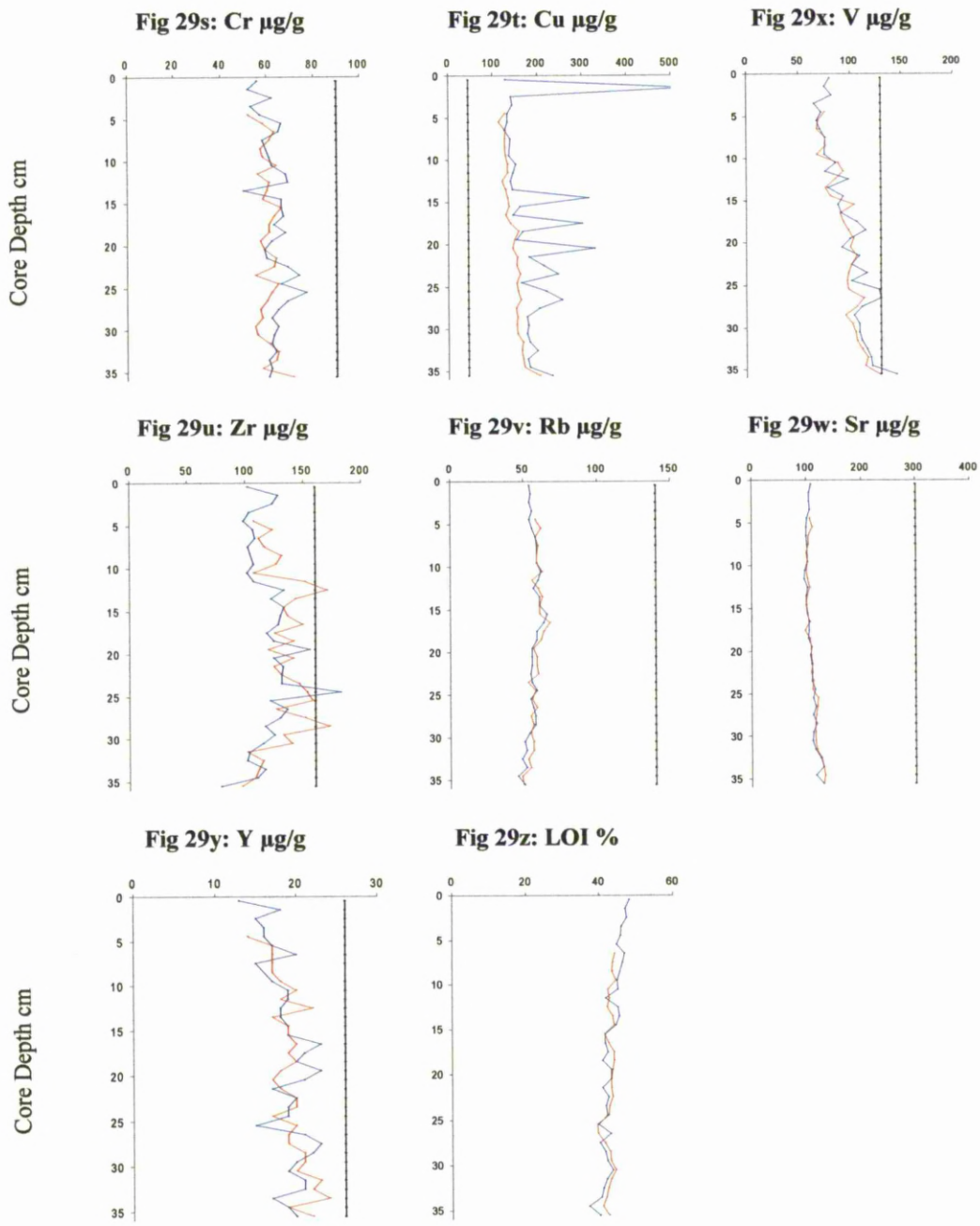


Figure 29a-z: Speke Hall Lake Element Concentrations. Average Shale Values (ASV) are shown in black as an indicator of unpolluted background sediment metal levels. The data shown in blue is from lake sediment samples that have been extracted for PCB and PAH analysis before the metal data were collected and the data shown in red is from sediment that had not been extracted for PCBs and PAHs.

7.3 Comparison of the Treated and Untreated Samples

The two sets of metal data were compared using a matched pair T-test and a Wilcoxon Matched Pair Test (Table 3). The metals that did not show a significant difference before and after extraction are highlighted in bold. There was a significant difference between the values of all the pre-extracted (treated) sediment and the untreated sediment except for Ba, Cd, Pb, Y and LOI.

	Matched Pair T Test			**Wilcoxon matched pairs test**	
	T	Significance (2 tailed)		Z	Asymp. Sig. (2-tailed)
Si treated – Si untreated	3.251	0.003		-2.841	0.004
Al treated – Al untreated	17.395	0.000		-4.860	0.000
Ti treated – Ti untreated	3.408	0.002		-3.331	0.001
Ca treated – Ca untreated	2.318	0.027		-2.430	0.015
Mg treated – Mg untreated	6.899	0.000		-4.370	0.000
K treated – K untreated	4.904	0.000		-3.959	0.000
Fe treated – Fe untreated	8.169	0.000		-4.860	0.000
Mn treated – Mn untreated	7.649	0.000		-4.840	0.000
S treated – S untreated	8.176	0.000		-4.782	0.000
P treated – P untreated	12.435	0.000		-4.860	0.000
As treated – As untreated	3.238	0.003		-3.028	0.002
Ba treated – Ba untreated	0.716	**0.479**		-0.696	**0.486**
Br treated – Br untreated	7.126	0.000		-4.796	0.000
Cd treated – Cd untreated	0.061	**0.951**		-0.019	**0.985**
Cr treated – Cr untreated	3.225	0.003		-2.879	0.004
Cu treated – Cu untreated	4.510	0.000		-4.843	0.000
Hg treated – Hg untreated	3.470	0.002		-3.067	0.002
Ni treated – Ni untreated	5.234	0.000		-4.297	0.000
Pb treated – Pb untreated	-1.080	**0.289**		-1.060	**0.289**
Rb treated – Rb untreated	-2.988	0.006		-2.646	0.008
Sr treated – Sr untreated	-2.885	0.007		-2.835	0.005
V treated – V untreated	2.812	0.009		-2.858	0.004
Y treated – Y untreated	0.069	**0.945**		-0.340	**0.734**
Zn treated – Zn untreated	7.453	0.000		-4.860	0.000
Zr treated – Zr untreated	-3.176	0.003		-3.036	0.002
LOI treated – LOI untreated	-0.502	**0.619**		-0.882	**0.378**

Table 3: T-test and Wilcoxon matched pair test results for metal extraction comparison.

7.4 Speke Hall Lake Magnetics Data

Magnetic Susceptibility (χ) (Fig 30a), Kappa Susceptibility (Fig 30a), Soft (Fig 30i) and SIRM (Fig 30b) show a slight decrease in the top layers of the core followed by an increase to 27-28cm at which point they begin to decrease downcore. SIRM fluctuates more than χlf and Kappa. HIRM (Fig 30g) exhibits a similar trend to SIRM. All these parameters are measurements of magnetic concentrations within the sediment. Soft and SIRM are measures of the amount of magnetite found, whilst HIRM and Hard% (Fig 30h) indicate the contribution of haematite and goethite.

χARM (Fig 30c), χARM/SIRM (Fig 30d) and χARM/χlf (Fig 30f) show similar downcore trends, with an initial decrease from the surface followed by an increase to 19-20cm followed by a decrease towards the bottom of the core. SIRM/χlf (Fig 30e) shows a similar pattern. These parameters can be used to assess the grain size of the sediment.

Hard% shows an overall downcore decrease but there is considerable variation throughout the core. FD% (Fig 30j) fluctuates considerably downcore and is a measure of the paramagnetic and superparamagnetic content of the sediment.

IRM reverse (Fig 30k) values exhibit relatively constant downcore values and there is no evidence of any real backfield divergence. IRM can be used as an indicator of the concentration of iron sulphide in the sediment.

Fig 30a: χlf and Kappa (red) 10^{-8} m^3 kg^{-1}

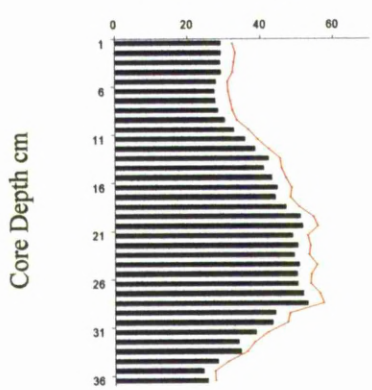


Fig 30b: SIRM 10^{-5} Am^2 kg^{-1}

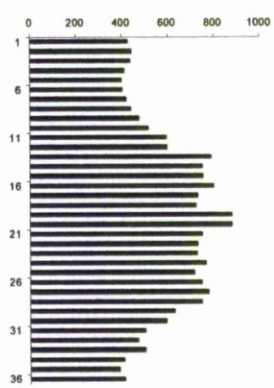
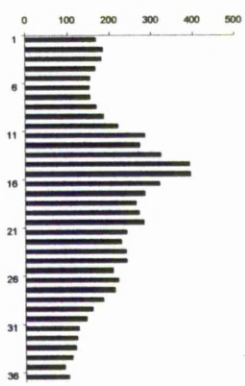


Fig 30c: χARM 10^{-8} m^3 kg^{-1}



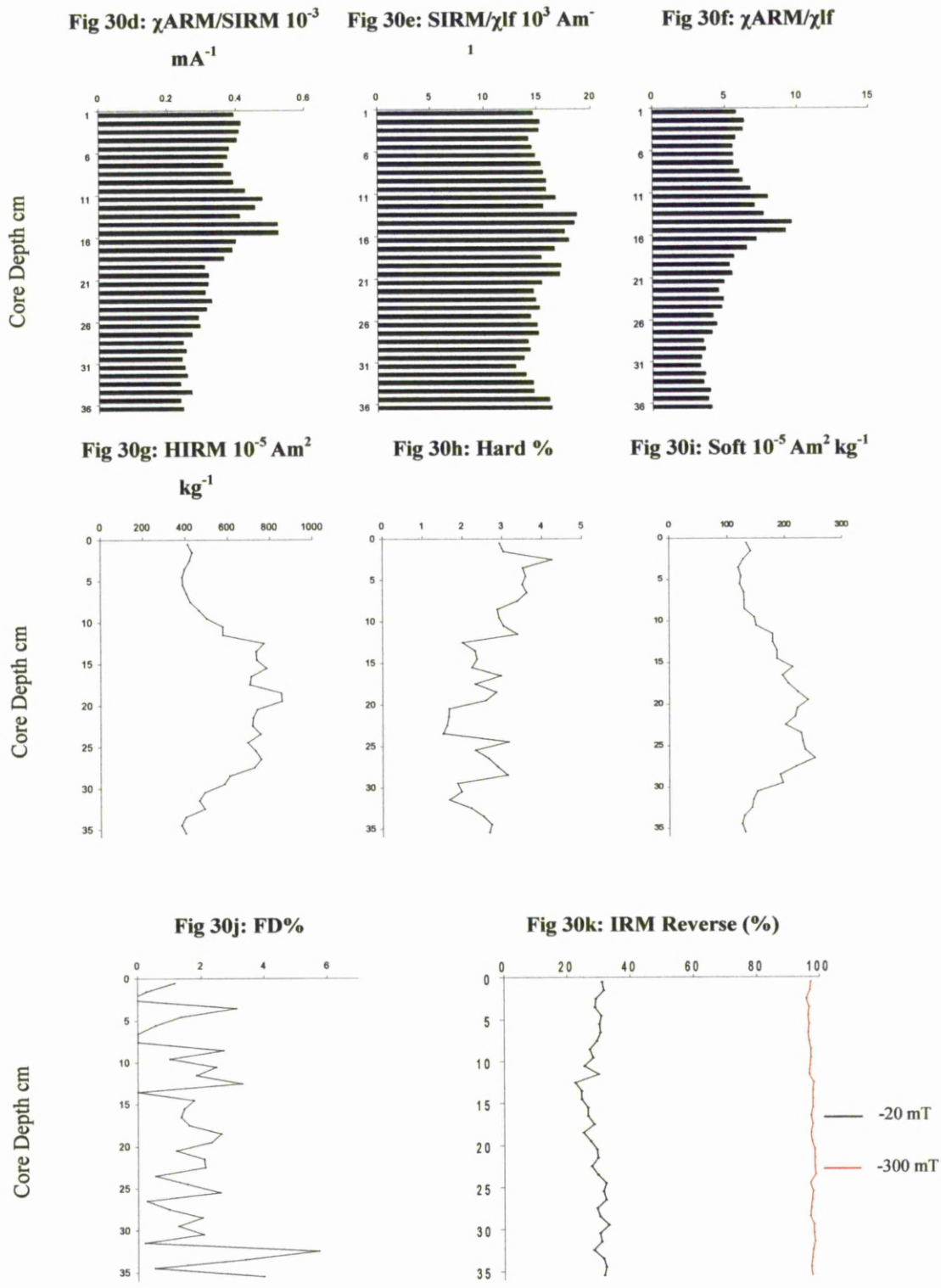


Figure 30a-k: Speke Hall Magnetics data.

7.5 Speke Hall Lake PCB Data

All PCBs (Figure 31a-u) exhibit an increase in concentrations towards the bottom of the part of the core. Between 10cm and 13cm they all show very low stable concentrations in the sediment and another low concentration in most PCBs can be seen at 19cm and 25cm. The final concentration at the bottom of the core seems to be decreasing overall. PCBs 18, 28, 52, 49 and 44 show an overall decrease to 10-11cm (with the exception of a peak at 8.5cm) followed by a stable profile between 10 and 13cm. they then show an increase in concentration to 18-19cm followed by another decrease to 25cm where they start to increase again towards the bottom of the core.

PCB 47, 105, 141 and 170 have much lower concentrations in the top part of the core and PCB 170 also exhibits very low concentrations between 18 and 25cm depth.

Figure 32 shows the downcore 5cm combined sample mean distribution of PCB congeners.

Figure 33 shows the mean 5cm combined % distribution of PCB chlorinated groups which are dominated by the tri, tetra and hexa chlorinated congeners.

Fig 31a: PCB 18 ng/g

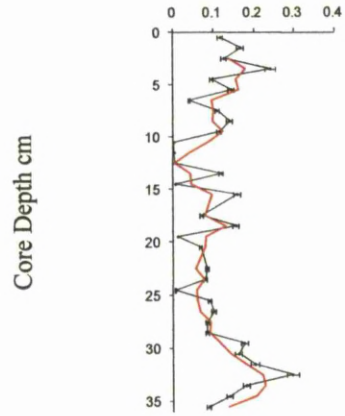


Fig 31b: PCB 28 ng/g

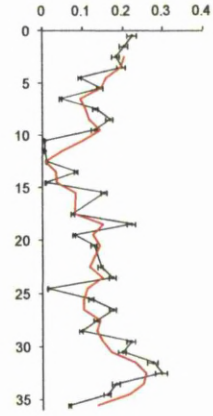


Fig 31c: PCB 44 ng/g

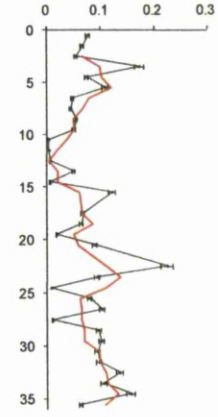


Fig 31d: PCB 47 ng/g

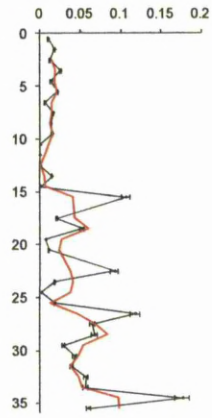


Fig 31e: PCB 49 ng/g

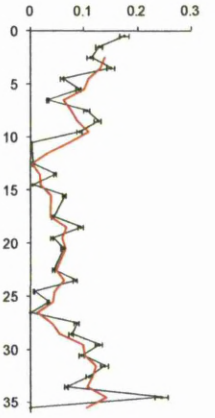
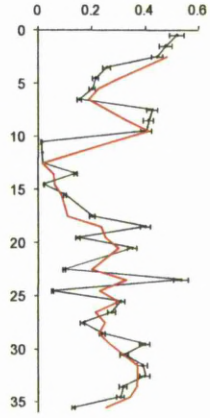


Fig 31f: PCB 52 ng/g



Core Depth cm

Fig 31g: PCB 66 ng/g

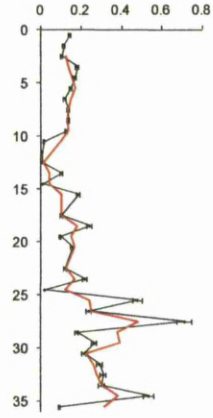


Fig31h: PCB 101 ng/g

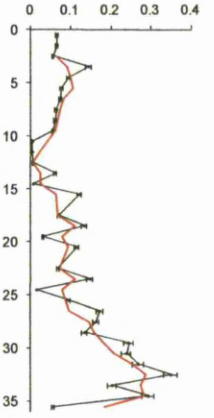
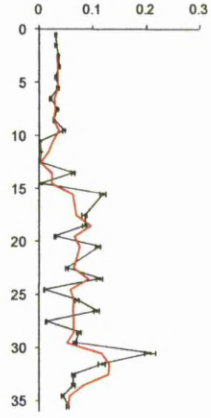


Fig 31i: PCB 105 ng/g



Core Depth cm

Fig 31j: PCB 118 ng/g

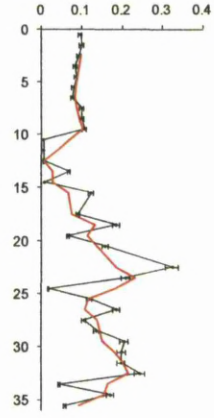


Fig 31k: PCB 128 ng/g

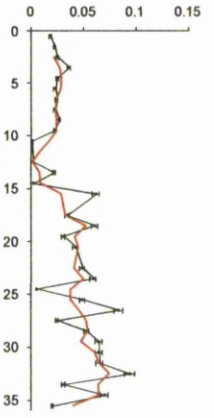
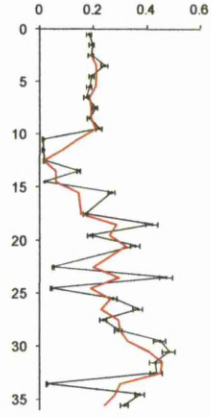


Fig 31l: PCB 138 ng/g



Core Depth cm

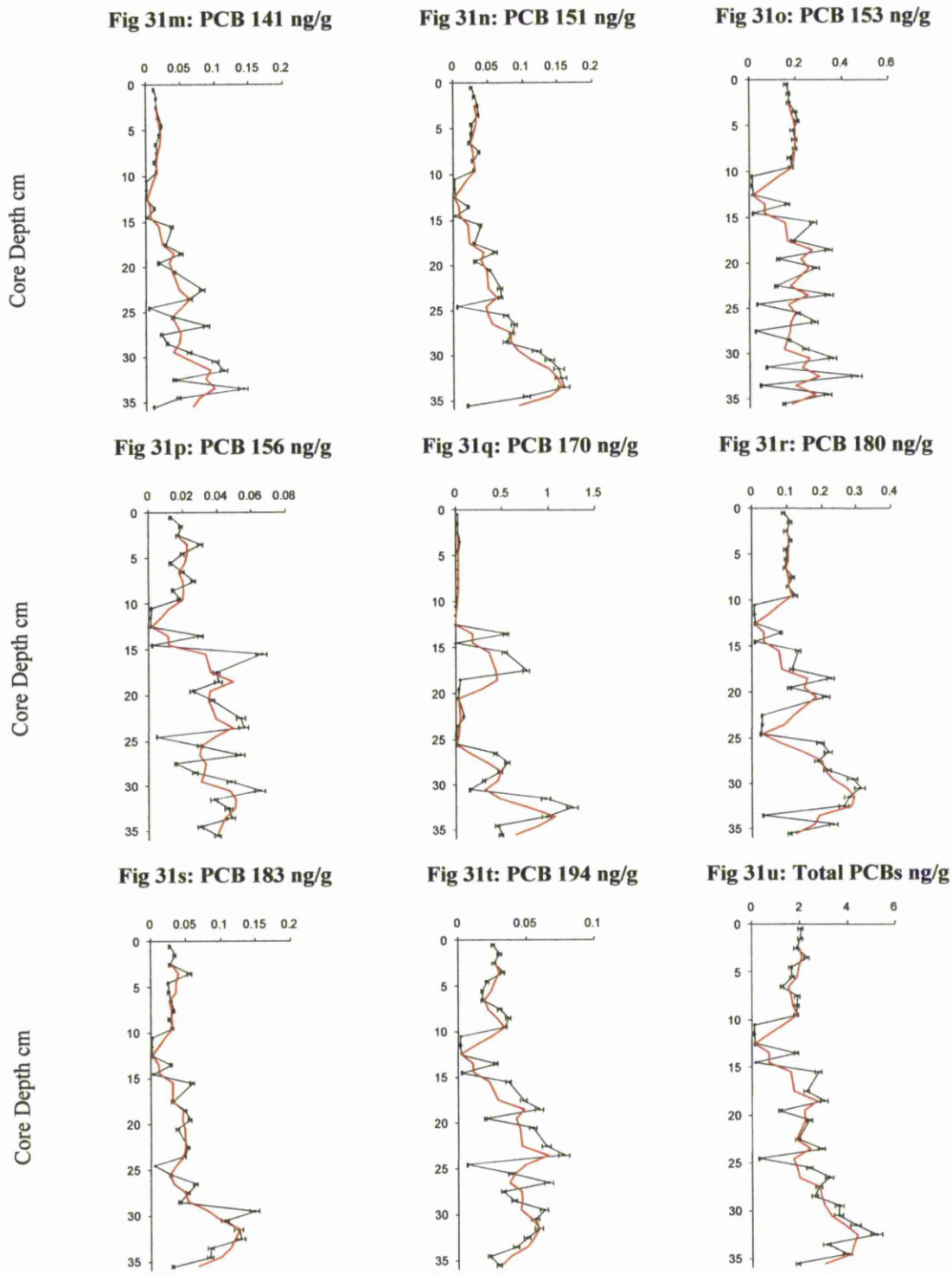


Figure 31a-u: PCB concentrations are shown in black and the general downcore trends can be seen as a 3 point running mean in red.

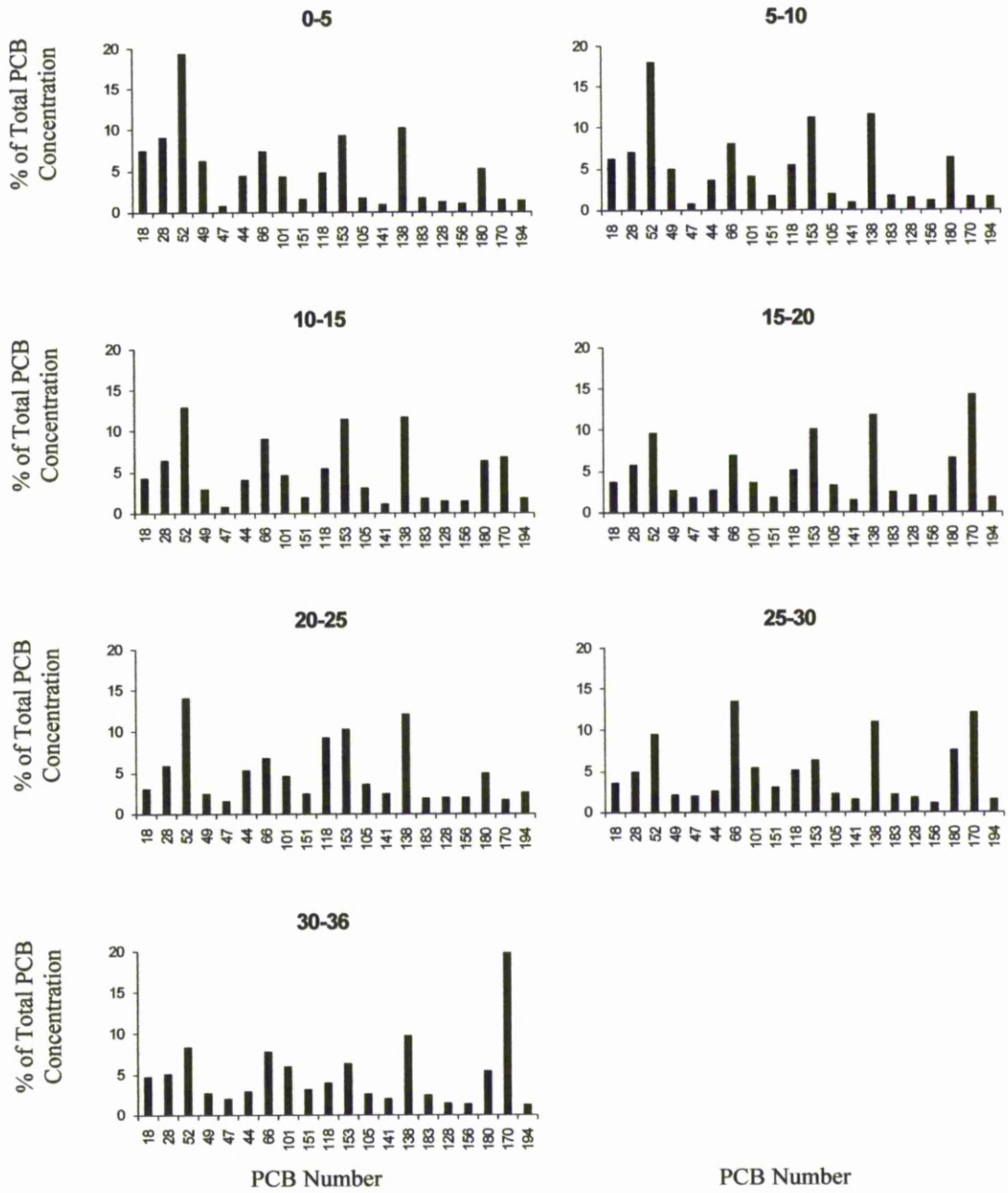


Figure 32: Downcore % Variation of PCB congeners. Values were calculated by combining a number of downcore sections and calculating mean % of the Total PCB concentration of each congener.

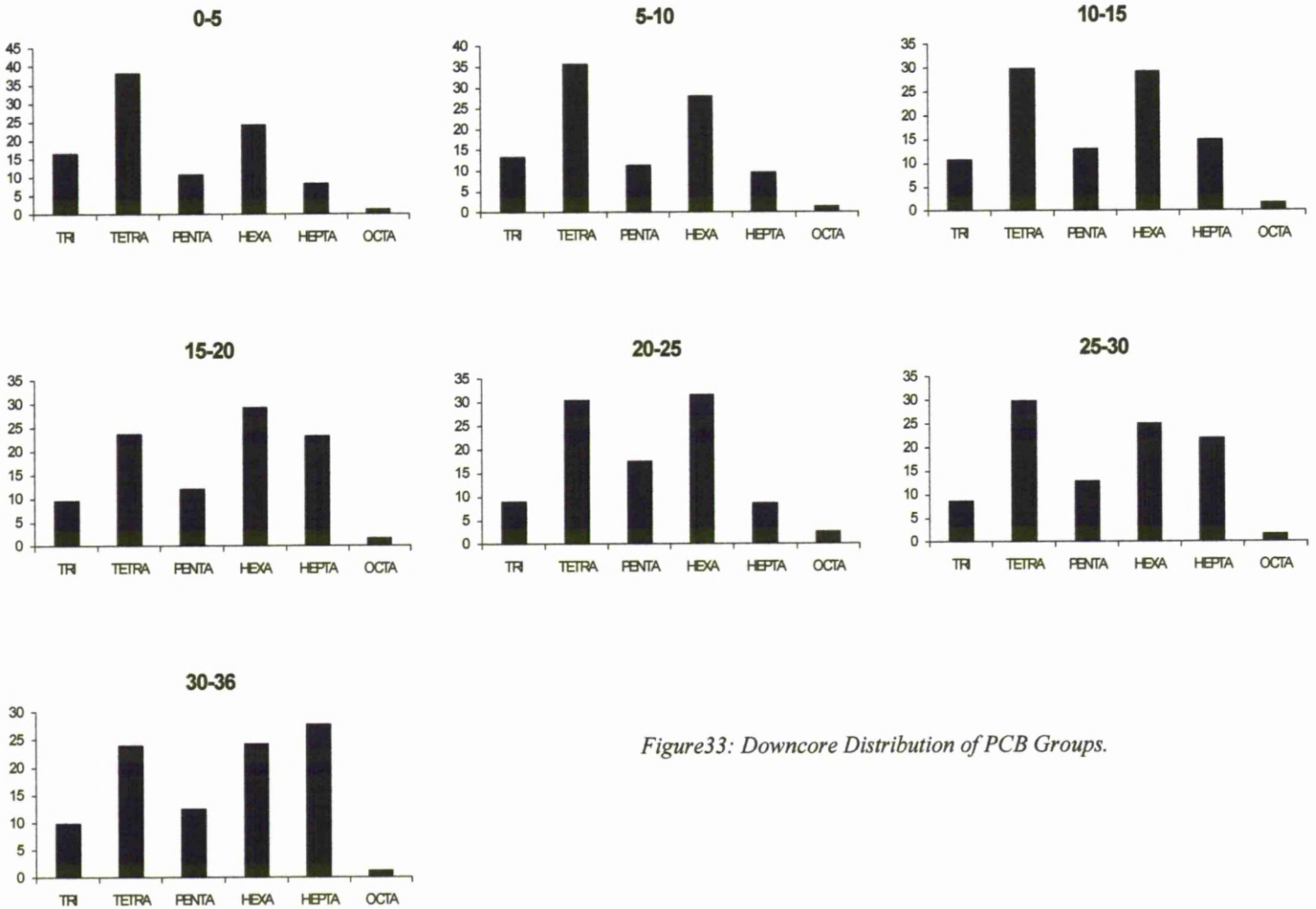


Figure33: Downcore Distribution of PCB Groups.

7.6 Speke Hall Lake PAH Data

7.6.1 PAH Downcore Distribution

PAH concentrations fluctuate downcore (Figure 34a-o). However, there appears to be an overall increase in concentrations to around 30cm depth at which point they appear to start to decrease.

Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenz[ah]anthracene seem to exhibit similar trends with decreases in concentrations at 8cm, 13cm, 19cm, 22cm and 32cm. This trend can also be seen in Acenaphthene and Fluorene, although it is not as obvious.

Fig 34a: Acenaphthene µg/g

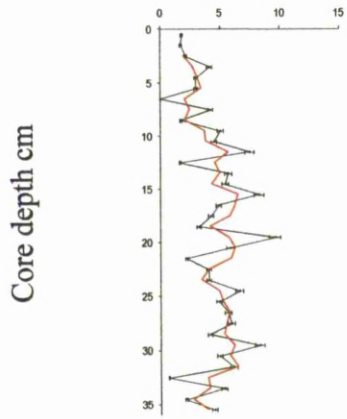


Fig 34b: Fluorene µg/g

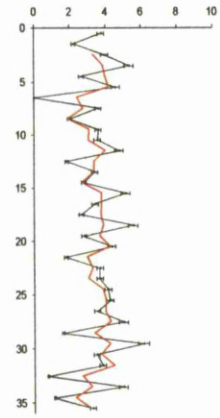


Fig 34c: Phenanthrene µg/g

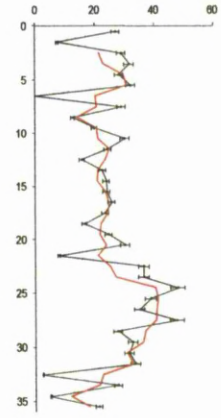


Fig 34d: Anthracene µg/g

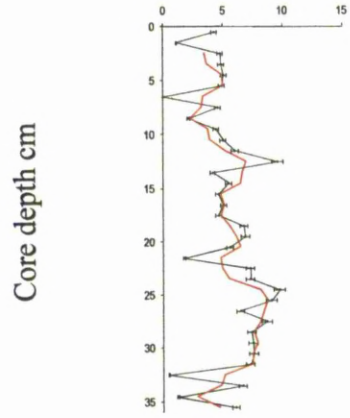


Fig 34e: Fluoranthene µg/g

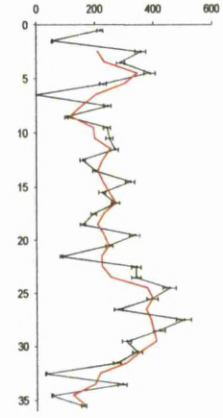
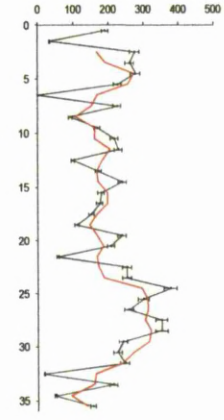


Fig 34f: Pyrene µg/g



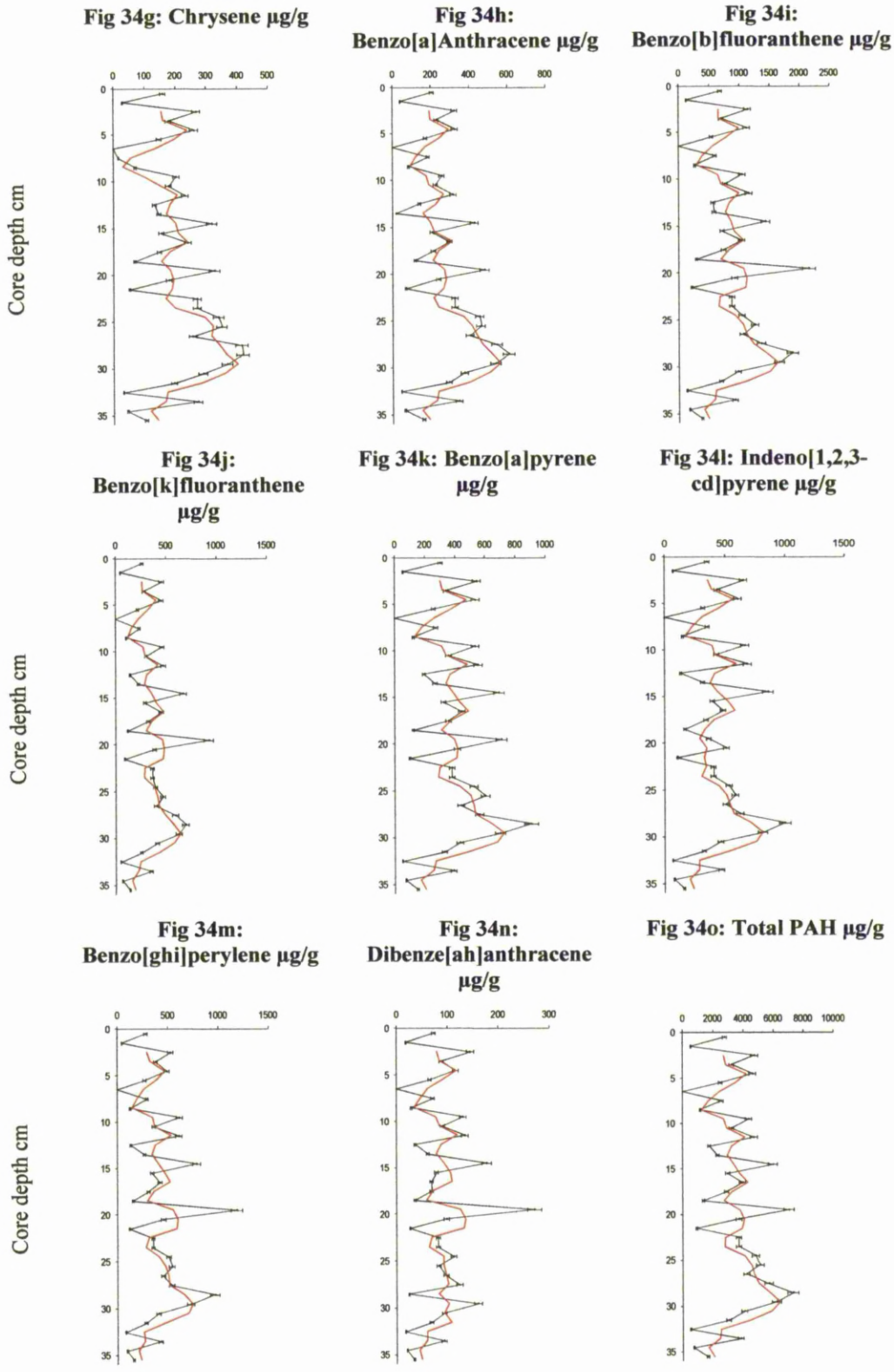


Figure 34a-o: PAH concentrations are shown in black and the general downcore trends can be seen as a 3 point running mean in red.

Figure 35 shows the mean 5cm sample downcore PAH percentage distribution dominated by the higher molecular weight PAHs.

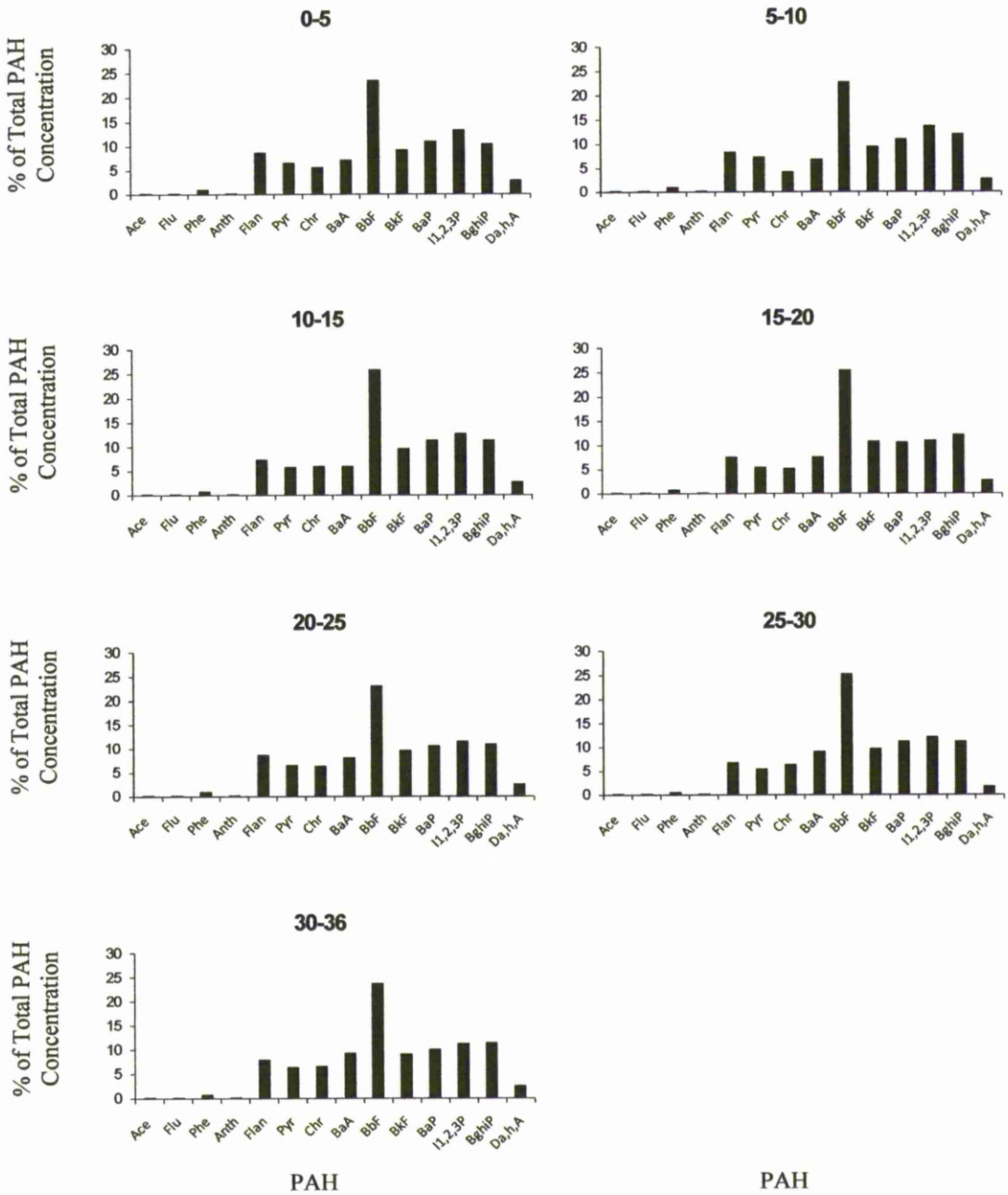


Figure 35: % downcore distribution of PAHs. Values were calculated by combining a number of downcore sections and calculating mean % of the Total PAH concentration of each individual PAH.

7.6.2 PAH Ratios

PAH ratios (Figure 36a-i) have been used to in an attempt to identify the potential sources of PAHs into the environment.

The Indeno[1,2,3-cd]pyrene/ (indeno[1,2,3,-cd]pyrene + Benzo [ghi] perylene) ratio is fairly stable downcore except for a major decrease at 20cm. Fluorene/(Fluorene + Pyrene) exhibits peak at 2cm, 18cm and a increase at the very bottom of the core. Benzo[a]pyrene/ (Benzo[a]pyrene + Chrysene) decreases slightly downcore with the exception of peaks at 7cm and 14cm. Fluoranthene/Pyrene fluctuates downcore. Benzo[b]fluoranthene/ Benzo[k]fluoranthene is fairly stable downcore except for a large peak at 12cm. Benzo[a]pyrene/ Benzo[ghi]perylene shows a slight overall downcore decrease but has a large peak at 12cm and a large dip at 19cm. Pyrene / Benzo[a]pyrene fluctuates downcore. Indeno[1,2,3-cd]pyrene/ Benzo[ghi]perylene shows an overall downcore decrease with a major dip at 19cm. CPAH/TPAH shows a fairly steady downcore trend with a slight dip at 19cm and a small peak at 29cm.

Fig 36a: Indeno[1,2,3-cd]pyrene/ (indeno[1,2,3,-cd]pyrene + Benzo [ghi] perylene)

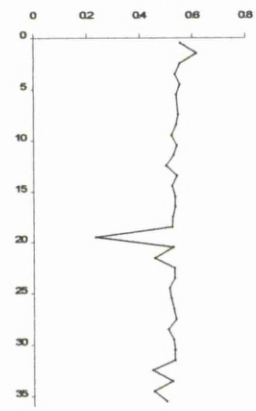


Fig 36b: Fluorene/(Fluorene + Pyrene)

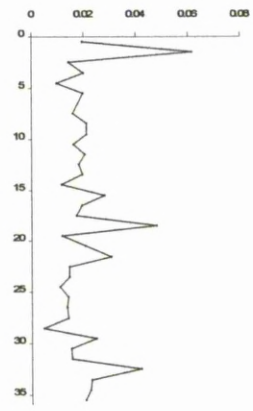
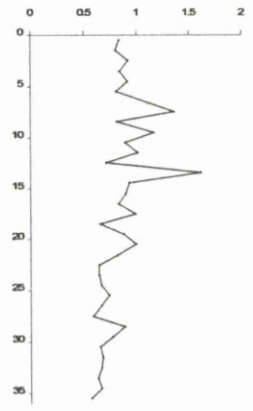


Fig 36c: Benzo[a]pyrene/ (Benzo[a]pyrene + Chrysene)



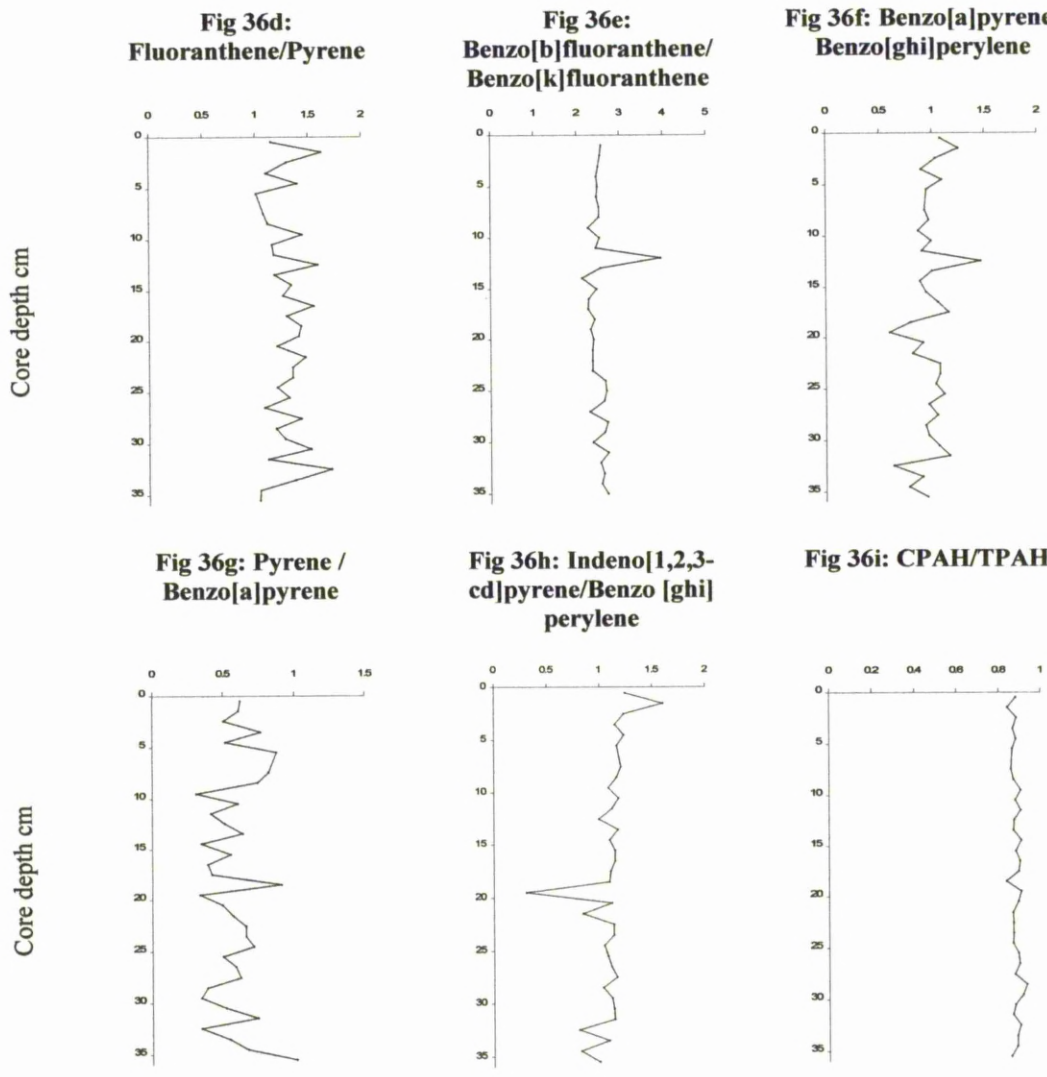


Figure 36: Speke Hall Lake PAH ratios (CPAH = sum of non-alkylated compounds (Fluorene + Pyrene + Benzo[a]anthracene + Chrysene + Benzo[b]fluoranthene + Benzo[k]fluoranthene + Benzo[a]pyrene + indeno[1,2,3-cd]pyrene + benzo[ghi/perylene).

7.7 Speke Hall Lake Organic Matter Data

TOC % is an indication of the levels of organic carbon in the sediment and C/N is a ratio showing how the levels of organic carbon and nitrogen change with depth. TOC % shows a similar profile (albeit with a little more fluctuation in values) to LOI except for in the first 5cm, where it shows a downcore increase and LOI shows a decrease. C/N ratio shows a downcore increase (Fig 37).

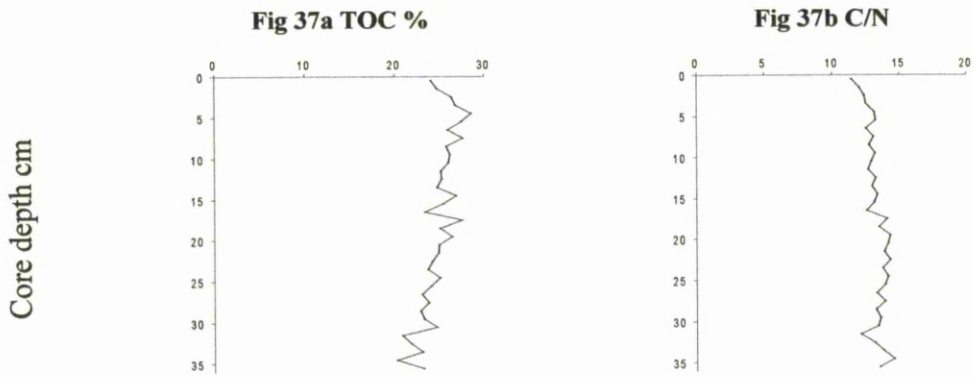


Figure 37: Speke Hall TOC and C/N data.

7.8 Speke Hall Correlations

Positive and negative correlations were considered at both 0.01 and 0.05 levels of significance. SPSS highlighted both strong correlations and those with a weaker but significant link. Correlations were taken to be strongly significant if they were over 0.7, i.e. 49% or more of the variance could be explained by the correlation rather than by coincidence. However, weaker correlations (under 0.7) that have been highlighted by SPSS as showing a significant relationship within the data have also been discussed. All the metal correlations discussed here are for the 'untreated' sediment cores.

7.8.1 Speke Hall Lake Element Correlations (See appendix 1)

Si shows a weak but positive correlation at the 0.01 significance levels with the Al and a negative but weak correlation with LOI. At the 0.05 significance level Si shows a weak positive correlation with Ti, Mg and Zr.

Al shows a weak positive correlation at the 0.01 level with Si and a strong positive correlation with Mg, It also shows a weak positive correlation at the 0.05 level of significance with Ti, K, χARM SIRM/χlf, ARM and a weak negative correlation with -20mT and Pyrene.

Ti shows a weak but positive correlation with Zr, χARM, Kappa, χlf, HIRM, SIRM, ARM and soft, a strong positive correlation with K, a weakly negative correlation with Mn and P and strong negative correlation with S at the 0.01 significance level. At the 0.05 level of significance it shows a weak positive correlation with Si, Al, Rb, % sand, and % fine sand and is weak negative one with Cu, Sr, -20mt, % Mud, % coarse silt, % medium silt, % fine silt and % clay.

Ca is shows a weak positive correlation with S, Y, -20mT, PCB 47, PCB 66, PCB 101, PCB 138, PCB 183, PCB 180 Total PCB, % mud, % very fine sand, % coarse silt, % medium silt, % fine silt, % very fine silt, % clay, a strong positive one with Mn, As, Ba, Cd, Cu, Ni, Sr, V, Zn, Soft/ARM, SIRM/ARM, % very coarse silt, a weak negative correlation with Rb, LOI, χARM, ARM, mean grain size, % sand, % coarse sand, % medium sand, % fine sand and a strong negative one with K, TOC, χARM/χSIRM, χARM/χlf at the 0.01 significance level. At the 0.05 significance level Ca shows a weak positive correlation with %FD, PCB 141, PCB 128, PCB 170, weakly negatively with Ti and SIRM/χlf.

At the 0.01 level of significance Mg shows a weak positive correlation with χARM/χlf, % medium sand, a strong positive correlation with Al and a weak negative one with soft/ARM, % very fine sand and PCB 118. At the 0.05 level it shows a weak positive correlation with Si, K, Rb, χARM/SIRM, SIRM/χlf and a weak negative correlation with Ba, SIRM/ARM, -20mT, PCB 66, PCB 101, PCB 138, PCB 128, PCB 180, Anthracene, Fluoranthene and Benzo[a]anthracene.

K shows a weak positive correlation at the 0.01 level with Zr, SIRM, χARM, SIRM/χlf, χARM/SIRM, χARM/χlf, HIRM, ARM, Mean grain size, % sand, % coarse sand, % medium sand, % fine sand, TOC, a strong positive correlation with Ti and Rb and a weak negative correlation with P, As, Ba, Pb, V, -20mT, % mud, % very fine sand, % very coarse silt, % coarse silt, % medium silt, % fine silt, % very

fine silt, % clay, and a strong negative correlation with Ca, Mn, S, Cd, Cu, Ni, Sr, Zn, SIRM/ARM, and soft/ARM. At the lower 0.05 significance level it shows a weak positive correlation with Al and Mg and a weak negative one with Fe, Y, PCB 47, PCB 66 and PCB 101.

Fe shows a weak positive correlation at the 0.01 level with Mn, P, As, Br, Cd, Cr, Cu, Ni, Zn, % mud, % very coarse silt, % coarse silt, % medium silt, % fine silt, % very fine silt, % clay, a strong positive correlation with S, a weak negative one with Zr, mean grain size, Kurtosis, % sand, % very coarse sand, % coarse sand, % medium sand, % fine sand, phenanthrene, fluoranthene and pyrene At the 0.05 significance level it shows a weak positive correlation with Ca, Ba, V, Y, FD% and a weak negative correlation with K, Kappa, χlf, soft, anthracene, chrysene, benzo[a]anthracene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and Total PAH.

Mn shows a weak positive correlation (at the 0.01 level) with Fe, As, P, Ba, Pb, V, Y, PCB 47, -20mT, Soft/ARM, % very fine sand, % very fine silt, a strong positive correlation with Ca, Cu, S, Cd, Ni, Sr, Zn, % mud, % very coarse silt, % coarse silt, % medium silt, % fine silt, % Clay. It also shows a weak negative correlation with Ti, Zr, Kappa, χlf, SIRM, χARM, χARM/SIRM, χARM/χlf, HIRM, ARM, SIRM/ARM, Kurtosis, % very coarse sand, % medium sand, % fine sand and a strong negative correlation with K, Rb, mean grain size, % sand % coarse sand and TOC. At the 0.05 level of significance it shows a weak positive correlation with Cr, PCB 66, PCB 101, PCB 170, total PCB and %FD and a weak negative one with Soft and skewness.

S shows a weak positive correlation at the 0.01 level with Ca, Cd, Cu, Ni, Sr, Zn, SIRM/ARM, Soft/ARM, % mud, % very coarse silt, % coarse silt, % medium silt, % fine silt, % very fine silt, % clay, a strong positive one with Fe, Mn, P, a weak negative correlation with Rb, Zr, SIRM, χARM, χARM/SIRM, χARM/χlf, HIRM, ARM, Soft, mean grain size, kurtosis, % sand, % very coarse sand, % coarse sand, % fine sand and TOC and a strong negative correlation with Ti, K and Kappa. It also shows a weak positive correlation at the 0.05 level with Pb, V, Y, FD%, sorting and a weak negative one with Skewness, Phenanthrene, Anthracene, Fluoranthene, Pyrene,

Chrysene, Benzo[a]anthracene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[ghi]perylene and Total PAH.

At the 0.01 significance level P shows a weak positive correlation with Fe, Mn, % medium silt, % fine silt and a strong positive correlation with S. At this level, it also shows a weak negative correlation with Ti, K, Zr, Kappa, χlf, SIRM, HIRM, χARM. ARM, Sorting and Kurtosis. At the lower level of significance (0.05) it shows a weak positive correlation with Sr, % mud, % coarse silt, % very fine silt and % clay and a weak negative correlation with skewness, % sand, % coarse sand and % fine sand.

Ba shows a weak positive correlation at the 0.01 level with Mn, Pb, Y, PCB 105, PCB 141, PCB 138, PCB 183, PCB 128, PCB 156, PCB 180, PCB 194, Total PCB, % very fine sand, % very coarse silt, % mud. It shows strongly positive correlations with Ca, As, Cd, Cu, Ni, Sr, V, Zn, SIRM/ARM, soft/ARM. Ba shows weak negative correlations with K, Rb, LOI, χARM/SIRM, χARM/χlf, HARD %, ARM, mean grain size, % coarse sand, % medium sand, % sand and a strong negative correlation with TOC. At the 0.05 level of significance it shows a weak positive correlation with Fe, S, -20 mT, -300mT, PCB 28, PCB 66, PCB 101, PCB 118, % coarse silt, % medium silt, % fine silt, % clay and a weak negative one with Mg and χARM.

Br shows a weak positive correlation at the 0.01 level of significance with Fe and a weak negative one with Zr.

Pb is strong positively correlated at the 0.01 level with As, Cu, Cd, Ni, Sr, V, Zn and SIRM/ARM and soft/arm and weakly positively correlated with Ca, Mn Ba, Y, -300mT, PCB 101, PCB 138, PCB 183, PCB 128, PCB 156, PCB 170, Total PCB, % very fine sand, % very coarse silt % mud. It shows weak negative correlations with K, Rb, Hard %, mean grain size, % coarse sand, % medium sand, % sand, TOC and a strong negative correlation with χARM/SIRM and χARM/χlf. At the 0.05 level of significance it shows a weak positive correlation with S, PCB 28, PCB 47, PCB 66, PCB 118, PCB 105 PCB 141, PCB 180, PCB 194,-20mt, % clay and a weak negative one with LOI, χARM, SIRM/χlf and ARM.

Arsenic shows the following positive weak correlations at the 0.01 level of significance: Fe, Mn, Ba, Y, SIRM/ARM, Soft/ARM, PCB 141, PCB 156, PCB 170, % very fine sand, % very coarse silt. It shows strong positive correlations with Ca, Ba, Cd, Cu, Ni, Pb, Sr, V and Zn. Weak negative correlations can be seen with K, Rb, χARM/SIRM, χARM/χLF, HARD%, LOI, mean grain size, % medium sand, % coarse sand and a strong negative correlation with TOC. At the 0.05 level it shows a weak positive correlation with S, -20mT, -300mT, % mud, % clay, PCB 47, PCB 66, PCB 101, PCB, 105, PCB 183, PCB 128, PCB 194 and Total PCB and a weak negative one with % sand and % very coarse sand.

Cd shows strong positive correlations at the 0.01 significance level with Ca, Mn, As, Ba, Cu, Ni, Pb, Sr, V, Zn, SIRM/ARM, Soft/ARM, % mud, % very fine sand, % very coarse silt, weaker positive correlations with Fe, S, Y -20mT, PCB 47, PCB 101, PCB 141, PCB 138, PCB 183, PCB 128, PCB 156, PCB 170, Total PCB, % coarse silt, % medium silt, % very fine silt, % fine silt, % clay. At this level of significance it shows a strong negative correlation with K, Rb, χARM/SIRM, χARM/χlf, TOC, % sand, % coarse sand, % medium sand and a weak negative correlation with LOI, ARM, χARM. At the lower 0.05 level of significance it shows a weak positive correlation with PCB 18, PCB 28, PCB 44, PCB 66, PCB 118, PCB 180, PCB 194 and a weak negative one with SIRM/χlf, % fine sand and % very coarse silt.

Zn shows strong positive correlations at the 0.01 level with Ca, Mn, As, Ba, Cd, Cu, Ni, Pb, Sr, V, Soft/ARM, SIRM/ARM, % very fine sand, % very coarse silt. It shows a weak positive correlation with Fe, S, Y, -20mT, PCB 47, PCB 66, PCB 101, PCB 141, PCB 183, PCB 128, PCB 156, PCB 170, Total PCB, % MUD, % coarse silt, % medium silt, % fine silt, % clay. It shows a weak negative correlation with χARM, χARM/χlf, ARM, % sand and a strong negative one with K, Rb, χARM/SIRM, mean grain size, % coarse sand and TOC. At the 0.05 level of significance it shows a weak positive correlation with % very fine silt, FD% - 300mT, PCB 28, PCB 44, PCB 118, PCB138, PCB180, PCB 194 and a weak negative one with LOI, Hard % and % very coarse sand.

Ni has strong positive correlations at the 0.01 level with Ca, Mn, As, Ba, Cd, Cu, Sr, Pb, V, Zn, SIRM/ARM, Soft/ARM, % very fine sand, % very coarse silt, and weaker positive correlations with Fe, S, Y, PCB 47, PCB, 66, PCB 101, PCB 141, PCB 183, PCB 128, PCB 156, PCB 170, Total PCB, -20mT, % mud, % coarse silt, % medium silt, % fine silt, % clay. It is shows a weak negative correlation with Rb, LOI, χARM, χARM/χlf, ARM, % sand and a strong negative correlation with K, χARM/SIRM, TOC, mean grain size, % coarse sand, % medium sand. At the lower level of significance it shows a weak positive correlation with Cr, -300mT, %FD, PCB 28, PCB 44, PCB 118, PCB 105, PCB 138, PCB 194, % very fine silt and a weak negative one with Hard % and % very coarse sand.

Hg shows a weak negative correlation with PCB 18, PCB 28, PCB 44, PCB 101, PCB 118, PCB 105, PCB 141, PCB 183, PCB 128, PCB 156, PCB 194, and Total PCB. At the 0.05 level it shows a weak positive correlation with FD%, SIRM/ARM, % coarse silt and weakly negative with -20mT, Kurtosis, % coarse sand, PCB 52, PCB 153 and PCB 180.

Cr is shows a weak positive correlation at the 0.01 level with Fe and at the 0.05 level of significance it shows a weak positive correlation with Mn, As, Cu, Ni, V, Y %FD and PCB 47.

Cu has strong positive correlations at the 0.01 level with Ca, Mn, As, Ba, Cd, Sr, Pb, V, Zn, SIRM/ARM, Soft/χARM and weaker positive correlations with Fe, S, Y, PCB 47, PCB, 66, PCB 101, PCB 141, PCB 183, PCB 128, Total PCB, -20mT, % mud, % very fine sand, % very coarse silt. It is exhibits weak negative correlations with Rb, χARM, χARM/χlf, ARM, mean grain size, % sand, % coarse sand, % medium sand and strong negatively correlations with K, Cr, χARM/SIRM. At the lower level of significance shows a weak positive correlation with -300mT, PCB 138, PCB 156, PCB 180, PCB 170, PCB 194, % very coarse silt, % medium silt, % fine silt % clay and a weak negative one with LOI and Hard %.

V shows strong positive correlations at the 0.01 level with Ca, As, Ba, Cd, Cu, Ni, Pb, Sr, Zn, SIRM/ARM, Soft/ARM and weak positive correlations with Mn, Y, PCB 47, PCB 101, PCB 183, PCB 128, PCB 156, Total PCB. It shows a weak negative

correlation with K, Rb, Hard%, χARM/χlf, Kurtosis, TOC, % coarse sand and a strong negative one with χARM/SIRM. At the 0.05 level of significance it shows a weak positive correlation with Fe, S, FD%, -20mT, -300mT, PCB 44, PCB 118, PCB 141, PCB 138, PCB 170, PCB 194, % very coarse silt, % coarse silt, % medium silt, % clay, % mud and a weak negative one with LOI, mean grain size, % sand, % very coarse sand.

Rb shows a weak positive correlation at the 0.01 level with mean grain size, % sand, % coarse sand, % medium sand, χARM, χARM/SIRM, SIRM/χlf, ARM and TOC, a strong positive correlation with K, a weak negative correlation with S, As, Ba, Cu, Pb, V, % mud, % very fine sand, % very coarse silt, % coarse silt, % medium silt, % clay, SIRM/ARM, -20mT, a strong negative one with Cu, Mn, Cd, Bi, Sr, Zn, -300mT, PCB 66, PCB 101. At the 0.05 level it shows a weak positive correlation with % very coarse sand, SIRM, SIRM/χlf, HIRM, Mg and Ti. It is shows a weak negative correlation with % very fine silt, PCB 183, PCB 180, Total PCB.

Sr shows a weak positive correlation with S, Y, -20mT, PCB 47, PCB 66, PCB 101, PCB 183, % mud, % very fine sand, % very coarse silt, % coarse silt, % medium silt, % fine silt, % very fine silt, % clay and a strong positive correlation with SIRM/ARM, SOFT/ARM, Ca, Mn, As, Ba, Cd, Cu, Ni, Pb, V, Zn. It has weak negative correlations with % sand, % coarse sand, % medium sand, LOI and mean grain size and a strong negative one with K, Rb, χARM, χARM/SIRM, χARM/χlf, ARM, TOC at the 0.01 level. It shows a weak positive correlation with P, PCB 44, PCB 141, PCB 138, PCB 128 and PCB 180 and a weak negative one with Ti, SIRM/χlf and % fine sand at 0.05 level of significance.

Zr shows a weak positive correlation at the 0.01 level with Kappa, χlf, SIRM, HIRM, soft, Ti, K, % fine silt, % very fine silt and a weak negative one with Fe, Mn, S, P and Br. At the 0.05 level it shows a weak positive correlation with Si, χARM, ARM, % sand, % fine sand, % clay, Acenaphthene, Anthracene, Chrysene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene and total PAH and a weak negative correlation with Sorting, % mud, % coarse silt, % medium silt.

Y is shows a weak positive correlation with Ca, As, Ba, Cd, Cu, Ni, Pb, Sr, V, Zn, SIRM/ARM, -300mT, a strong positive correlation with Mn and a weak negative one with LOI, %FD, Hard %, mean grain size, kurtosis, % coarse sand and TOC at the 0.01 level. It shows a weak positive correlation with Al, Fe, S, Cr, Soft/ARM, % mud, % very coarse silt, % medium silt, % clay and a weak negative correlation with χARM/SIRM, % sand, % very coarse sand and TOC at the 0.05 level.

LOI shows a weak positive correlation at the 0.01 level with TOC. It is shows a weak negative one with Fe, Mn, S, P and Br. It shows a weak positive correlation with % medium sand and a weak negative one with Cd, Cu, Pb, Y, Zn. SIRM/ARM, Soft, Soft/ARM, % very fine sand and % very coarse silt at the 0.05 level.

7.8.2 Speke Hall Lake PCB Correlations (See appendix 1)

As in the Upper Marsh Core the PCBs show good (if weak) correlations amongst themselves. Many of the PCBs have positive correlation with magnetic indicators of the coarser grain size fraction (if not actually with the grain size fraction themselves).

PCB 18 shows a weak positive correlation with PCB 52, PCB 44, PCB 151, PCB 118, PCB 153, PCB 141, PCB 138, PCB 128, PCB 156, PCB 180, PCB 170, PCB 194 and Soft/χARM, a strong positive correlation with PCB 28, PCB 49, PCB 101, PCB 183 and Total PCB and a weak negative one with χARM, SIRM/χlf and ARM at the 0.01 level of Significance. At the 0.05 level it shows a weak positive correlation with PCB 47, PCB 66, PCB 105, SIRM/ARM, -20mT and a weak negative one with χARM/SIRM.

PCB 28 shows a weak positive correlation the 0.01 level with PCB 44, PCB 66, PCB 118, PCB 153, PCB 141, PCB 138, PCB 128, PCB 156, PCB 180, PCB 170, PCB 194, SIRM/ARM, -20mT, soft/χARM, a strong positive correlation with PCB 18, PCB 52, PCB 49, PCB 101, PCB 151, PCB 183, Total PCB and a weak negative one with χARM, χARM/SIRM, SIRM/χlf, χARM/χlf and ARM. At the 0.05 level it shows a weak positive correlation with PCB 47 and PCB 105.

At the 0.01 level PCB 52 shows a weak positive correlation with PCB 18, PCB 49, PCB 101, PCB 151, PCB 118, PCB 153, PCB 128, PCB 180, PCB 194, Total PCB, -

20mT, Soft/χARM and a strong positive one with PCB 28, It is also shows a weak negative correlation with χARM, SIRM/χlf, ARM. At the 0.05 level it shows a weak positive correlation with PCB 105 and PCB 183 and a weak negative one with χARM/ χlf and % coarse silt.

These trends are repeated amongst the other PCBs

Total PCB shows a weak positive correlation with PCB 18, PCB 28, PCB 52, PCB 44, PCB 101, PCB 151, PCB 153, PCB 105, PCB1 41, PCB 170, a strong positive one with PCB 118, PCB 138, PCB 183, PCB 128, PCB 156, PCB 180, PCB 194, a weak negative correlation with χARM, SIRM/χlf, ARM, -20mT and a strong negative one with χARM/SIRM, χARM/χlf, SIRM/ARM, soft/χARM at the 0.01 level. It shows a weak positive correlation with PCB 47, PCB 66, Benzo[a]anthracene and a weak negative correlation with TOC and % Coarse sand at the 0.05 level.

The majority of PCBs (PCB 28, 47, 44, 66, 101, 118, 105, 141, 138, 183, 128, 156, 180, 170, 194, Total PCB) show positive correlations with many of the 'pollutant' metals. Cd, Pb, Zn, Ni showing the greatest number of positive correlations with As, V and Cu also showing correlations with a number of PCBs. Ca, Ba and Sr also have positive correlations with a number of the PCBs, whilst Hg has negative correlations with many PCB (PCB 18, 28, 5244, 66, 101, 118, 153, 105, 141, 183, 128 156, 180, 194 and Total PCBs).

The only PCBs to show a correlation with PAHs are PCB 66, 101, 151, (with benzo[a]anthracene); 105 (with benzo[a]anthracene and chrysene) 138 (with benzo[a]anthracene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene); PCB 128 (with benzo[a]anthracene, anthracene, fluoranthene, chrysene), PCB 180 (with pyrene, chrysene, benzo[a]anthracene, phenanthrene, anthracene, fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[1,2,3-cd]pyrene and total PAH) and Total PCB with benzo[a]anthracene.

7.8.3 Speke Hall Lake PAH Correlations (See appendix 1)

As with the PCBs, PAHs show good correlations amongst themselves (although, again, some of these are weak) and many of them show a positive correlation with the coarser grain size fraction (% coarse sand and % very coarse sand) and a negative correlation with fines, which would suggest that there is a grain size influence on the PAH concentrations.

Acenaphthene shows a weak positive correlation at the 0.01 level with fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1.2.3-cd]pyrene, benzo[ghi]perylene, dibenz[a,h]anthracene, Total PAHs, Kappa, χlf, HIRM and a weak negative one with -20mT. It shows a weak positive correlation at the 0.05 level with χARM, SIRM/χlf and SIRM/ARM.

Fluorene shows a weak positive correlation at the 0.01 level with acenaphthene, phenanthrene, anthracene, fluoranthene, and pyrene and shows a weak positive correlation at the 0.05 level with chrysene, benzo[a]anthracene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, Total PAHs and % fine sand.

Phenanthrene shows a weak positive correlation with acenaphthene, fluorene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, dibenz[a,h]anthracene, Total PAHs, Kappa, χlf and soft. It is shows a strong positive correlation with anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, and at the 0.05 level of significance it shows a weak positive correlation with % very coarse sand, % fine sand and a weak negative one with % medium silt, % fine silt, % very fine silt and % clay.

At the 0.0 1 Level anthracene shows a weak positive correlation with acenaphthene, fluorene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, Total PAHs, Kappa, χlf and Soft and a strong positive one with phenanthrene, fluoranthene, pyrene, chrysene and benzo[a]anthracene. At the 0.05 level of significance it shows a weak positive correlation with dibenz[a,h]anthracene and HIRM.

Fluoranthene shows a weak positive correlation with acenaphthene, fluorene, dibenz[a,h]anthracene, Kappa, χlf, % very coarse sand and a strong positive one with phenanthrene, anthracene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and Total PAHs at the 0.01 level and it shows a weak positive correlation with HIRM and soft and a negative weak one with % medium silt, % fine silt, % very fine silt, % clay at the 0.05 level.

Total PAH shows a weak positive correlation with acenaphthene, phenanthrene, anthracene, Kappa, χlf, Soft and % very coarse sand and a strong positive correlation with fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1.2.3-cd]pyrene, benzo[ghi]perylene, dibenz[a,h,]anthracene at the 0.01 level. At the 0.05 significance level it shows a weak positive correlation with fluorene and HIRM and weakly negative one with % mud, % medium silt, % fine silt and % clay. As with the other core these trends are repeated between the other PAHs

TOC shows a weak positive correlation with % coarse sand, % medium sand, χARM/SIRM, χARM/χlf, Hard % and a weak negative correlation to % fine sand, % very coarse silt, SIRM/ARM, -300mT, Soft/ARM at the 0.01 level and it is also weakly positively correlated with % Sand, χARM, ARM and weakly negative with % mud, % coarse silt, % medium silt, % fine silt, % very fine silt and % clay at the 0.05 level of significance.

Many PAHs have a weak positive correlation with Zr which could be related to the grain size fraction correlations. Phenanthrene, anthracene, pyrene, chrysene, benzo[a]anthracene, benzo[a]pyrene and total PAHs have a positive correlations with Fe and S, whilst benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[ghi]perylene have a positive correlation with S and indeno[1,2,3-cd]pyrene has a positive correlation with Fe.

7.8.4 Speke Hall Magnetic Correlations (See appendix 1)

At the 0.01 level of Significance Kappa shows a weak positive correlation with χARM, ARM, -300 mT, a strong positive correlation with χlf, HIRM and Soft and a

weak negative one with Hard %. It also shows a weak negative correlation with % medium sand at the 0.05 level.

χlf shows a weak positive correlation with χARM, ARM, -300mT, a strong positive one with Kappa, HIRM and Soft and a weak negative one with Hard % at the 0.01 level. It also shows a weak negative correlation with % medium sand at the 0.05 level.

FD% shows a weak negative correlation with % coarse sand at the 0.01 level. It also shows a weak negative correlation with kurtosis at the 0.05 level.

SIRM shows a weak positive correlation with SIRM/χlf, ARM and -300 mT, a strong positive one with Kappa, χlf, HIRM and Soft and a weak negative correlation with Hard % and -20mT at the 0.01 level.

At the 0.01 level of significance χARM shows a weak positive correlation with Kappa, χlf, χARM/SIRM, a strong positive correlation with SIRM/χlf, χARM/χlf, HIRM and ARM. It shows a weak negative one with SIRM/ARM and strong negative one with -20mT and soft/χARM. It shows a weak positive correlation with % coarse sand at the 0.05 Level.

χARM/SIRM shows a weak positive correlation with % coarse sand, % medium sand, χARM, SIRM/χlf and ARM, strongly with χARM/χlf, a weak negative one with % very fine silt, % very coarse silt, -20mT and a strong negative correlation with SIRM/ARM and Soft/χARM at the 0.01 level. It shows a weak positive correlation with % sand and a weak negative one with % mud, % medium sand, % fine sand and % clay at the 0.05 level.

SIRM/χlf shows a weak positive correlation with χARM/SIRM and HIRM and a strong correlation with χARM, χARM/χlf and ARM, a weak negative one with SIRM/ARM and Soft/χARM and a strong negative one with -20mT at the 0.01 level.

χARM/χlf shows a weak positive correlation with % coarse sand and % medium sand, a strong positive one with χARM, χARM/SIRM, SIRM/χlf and ARM and a

weak negative correlation with % very fine sand and a strong negative correlation with SIRM/ARM, -20mT and soft/χARM at the 0.01 level of significance.

HIRM shows a weak positive correlation with SIRM/χlf, -300mT, a strong positive one with Kappa, χlf, χARM, ARM and Soft and a negative weak one with HIRM and -20mT at the 0.01 level.

Hard % shows a weak positive correlation with % coarse sand and % medium sand, a weak negative one with % very fine sand, Kappa, χlf, HIRM and soft and a strong negative one with -300mT.

ARM shows a weak positive correlation with Kappa, χlf, χARM/SIRM and Soft, a strong positive one with χARM, SIRM/χlf, χARM/χlf and HIRM, a weak negative correlation with SIRM/ARM and a strongly negative correlation with -20mT and Soft/ARM at the 0.01 level. It shows a weak positive correlation with % coarse sand at the 0.05 level.

SIRM/ARM shows a weak positive correlation with % mud, % very fine silt, % very coarse silt, % clay -20mT, a strong positive one with Soft/χARM, a negative weak one with % sand, % coarse sand, % medium sand, χARM, SIRM/χlf and ARM and a strong negative one with χARM/SIRM and χARM/χlf at the 0.01 level. It shows a weak positive correlation with % coarse silt, % medium silt, % fine silt and -300mT and a weak negative one with Hard % at the 0.05 level.

At the 0.01 level of significance Soft shows a weak positive correlation with χARM, ARM and -300mT and a strong positive one with Kappa, χlf and HIRM. It also shows a weak negative correlation with Hard % and at the 0.05 level it shows a weak negative correlation with % medium sand.

-20mT exhibits a positive weak correlation with SIRM/ARM and Soft/χARM and a negative weak one with χARM/SIRM and HIRM and a strong negative one with χARM, SIRM/χlf, χARM/χlf and ARM at the 0.01 level.

-300mT shows a weak positive correlation with % very fine sand, Kappa, χlf, HIRM, Soft, a negative weak correlation with % coarse sand, % medium sand and a strong negative one with Hard % at the 0.01 level. It is also weakly positive with % coarse silt and SIRM/ARM at the 0.05 level.

Soft/χARM shows a weak positive correlation with % mud, % very fine silt, % very coarse silt, -20mT, a strong positive one with SIRM/ARM, a negative weak correlation with % sand, % coarse sand, % medium sand, SIRM/χlf and a strong negative one with χARM, χARM/SIRM χARM/χlf and ARM at the 0.01 level. It shows a weak positive correlation with % medium silt % fine silt and % clay at the 0.05 level.

7.9 Principal Component Analysis Speke Hall Lake

Multivariate statistical analysis using Principal Component Analysis (PCA) was undertaken in an attempt to establish relationships between organic matter, grain size and pollutant inputs (PCBs, PAHs and heavy metals). The results of this are given below as a series of bivariate plots and associated eigenvectors and eigenvalues.

7.9.1 Speke Hall Lake Element, Organic Matter and Grain Size PCA

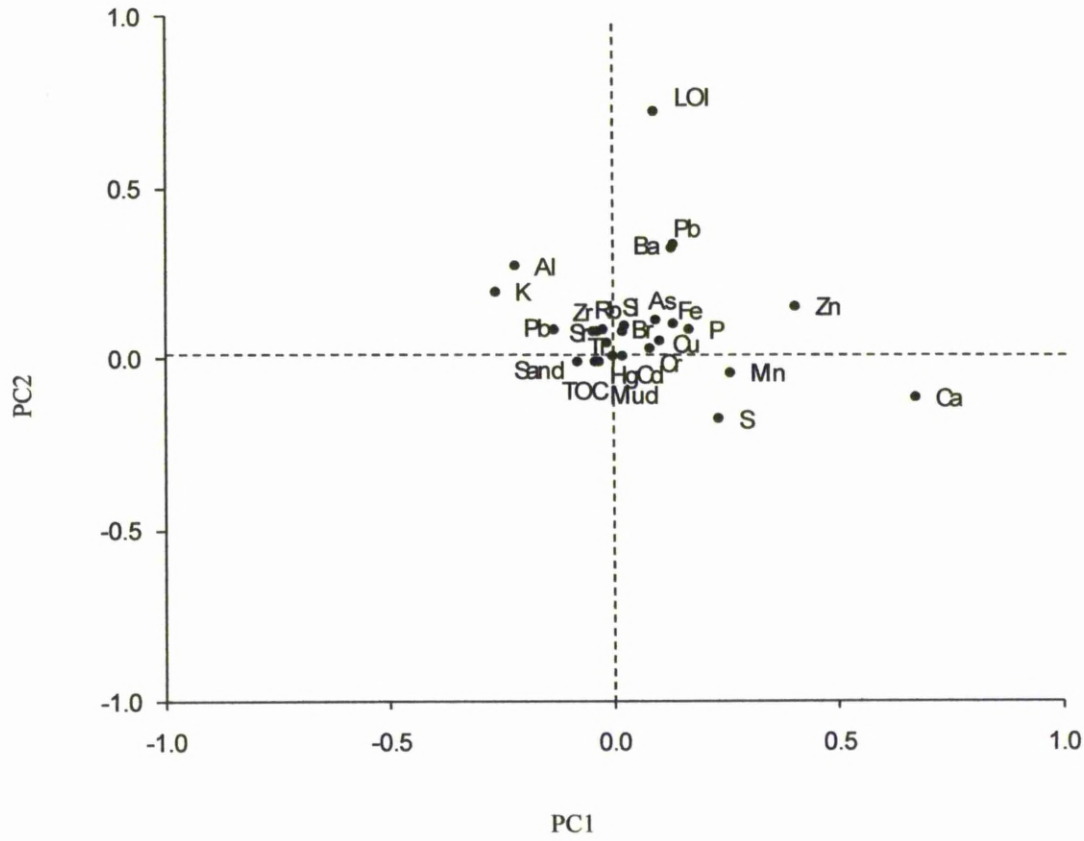


Figure 38: PCA Scatter plot of Eigenvectors comparing elements, organic matter and grain size. The relationship between PCA 1 (which explained 53.9% of the total variance) and PCA 2 (which explained a further 15.4%) is shown, along with graphical representations of the contributions of the original variables to both PC 1 and PC 2.

There appear to be three main groupings in this data lithogenic (Al, K, Ti, Mg), organic matter association (Ca, Mn, S) and Pollution metals (Pb, Zn, Hg, Cd, Ni, As).

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	1.03	53.9	53.9
2	0.293	15.4	69.2
3	0.204	10.7	79.9
4	0.171	9.0	88.9
5	6.62E-2	3.5	92.4

The first three components account for 80% of the variation

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Si	0.024	0.093	-0.496	-0.318	-0.021
Al	-0.219	0.273	-0.280	-0.016	0.183
Ti	-0.016	0.044	-0.060	-0.096	0.018
Ca	0.671	-0.117	-0.072	-0.216	-0.170
K	-0.264	0.199	-0.203	-0.220	0.220
Fe	0.132	0.100	-0.109	0.275	0.400
Mn	0.258	-0.042	-0.026	0.116	0.157
S	0.234	-0.180	-0.058	0.506	0.140
P	-0.134	0.084	0.024	0.193	0.171
As	0.094	0.113	-0.015	-0.067	0.069
Ba	0.127	0.326	0.098	-0.222	0.238
Br	0.021	0.079	0.034	0.023	0.160
Cd	0.021	0.004	0.000	-0.005	0.000
Cr	0.080	0.029	-0.070	-0.083	-0.003
Cu	0.102	0.052	0.014	-0.029	0.046
Hg	-0.003	0.004	-0.021	0.019	-0.003
Ni	0.169	0.084	-0.022	-0.068	0.040
Pb	0.131	0.334	0.118	-0.209	0.090
Rb	-0.025	0.086	0.209	0.140	0.043
Sr	-0.046	0.077	0.725	-0.257	0.111
Zn	0.405	0.153	-0.006	-0.102	0.068
Zr	-0.038	0.079	-0.079	-0.166	-0.215
LOI	0.091	0.720	0.026	0.421	-0.392
% Sand	-0.082	-0.010	0.013	-0.021	-0.466
% Mud	-0.042	-0.009	0.007	-0.008	-0.346
TOC	-0.033	-0.009	0.019	0.006	0.020

7.9.2 Speke Hall Lake PCB, Organic Matter and Grain Size PCA

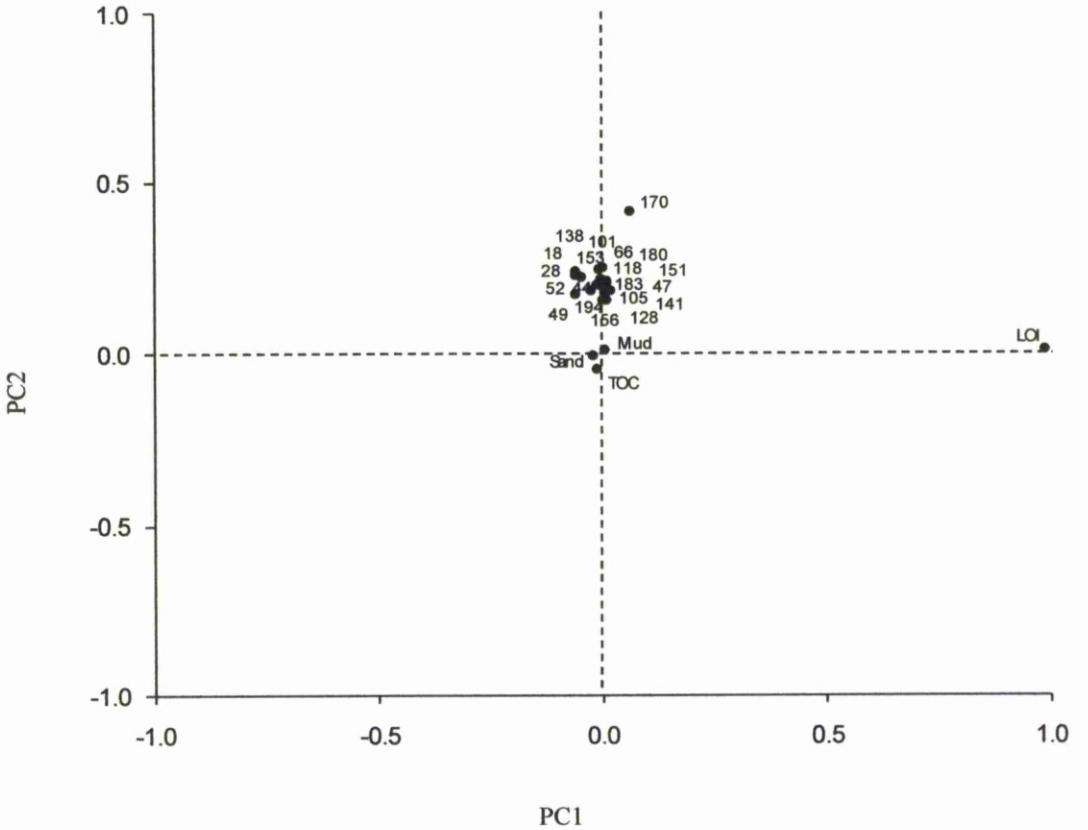


Figure 39: PCA Scatter plot of Eigenvectors comparing PCBs, organic matter and grain size. The relationship between PCA 1 (which explained 66.6% of the total variance) and PCA 2 (which explained a further 19.3%) is shown.

This first three components account for 90% of the variation and PCB behaviour seems to be related to PCB input rather than to other factors.

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	0.82	66.6	66.6
2	0.238	19.3	86.0
3	5.39E-2	4.4	90.4
4	3.85E-2	3.1	93.5
5	3.36E-2	2.7	96.2

Eigenvectors

(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
18	-0.059	0.240	0.028	-0.620	-0.108
28	-0.057	0.230	-0.046	-0.644	-0.145
52	-0.047	0.226	-0.174	-0.005	-0.244
49	-0.061	0.174	-0.404	-0.014	0.163
47	0.011	0.207	0.137	0.082	0.097
44	-0.024	0.188	-0.005	0.118	-0.034
66	0.000	0.252	-0.063	0.024	0.031
101	0.003	0.251	-0.035	0.055	0.046
151	0.011	0.215	-0.053	0.003	0.045
118	0.000	0.215	-0.102	0.100	-0.121
153	-0.013	0.204	-0.100	0.206	-0.269
105	0.013	0.182	-0.015	0.182	-0.095
141	0.018	0.187	-0.051	0.053	0.033
138	-0.006	0.246	-0.047	0.186	-0.299
183	0.003	0.199	-0.008	0.038	0.031
128	0.007	0.179	-0.039	0.100	-0.034
156	0.013	0.157	0.026	0.113	-0.046
180	-0.001	0.220	-0.038	0.137	-0.117
170	0.065	0.412	0.503	0.014	0.612
194	0.004	0.155	-0.033	0.066	-0.088
TOC	-0.010	-0.044	-0.042	-0.013	-0.045
LOI (%)	0.990	0.015	-0.078	-0.076	-0.058
% Sand	-0.019	-0.004	-0.572	-0.012	0.393
% Mud	0.006	0.011	-0.398	-0.019	0.344

7.9.3 Speke Hall Lake PAH, Organic Matter and Grain Size PCA

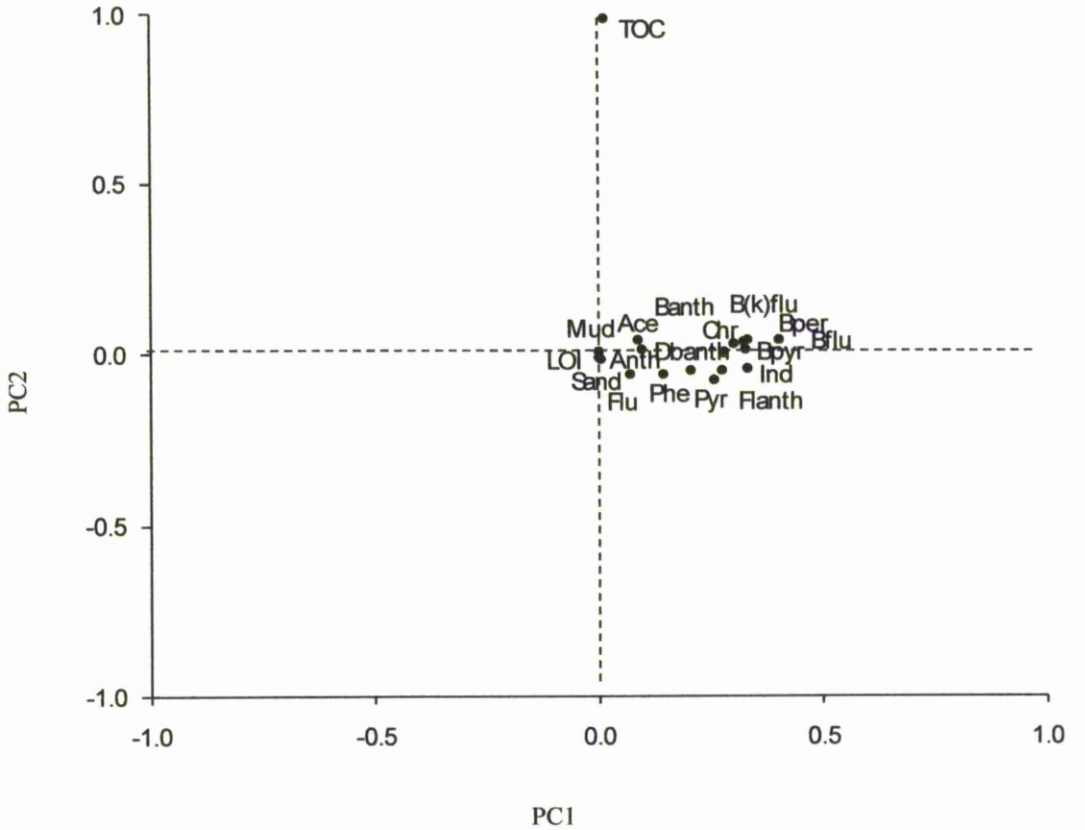


Figure 40: PCA Scatter plot of Eigenvectors comparing PAHs, organic matter and grain size. The relationship between PCA 1 (which explained 86.7% of the total variance) and PCA 2 (which explained a further 7.9%) is shown, along with graphical representations of the contributions of the original variables to both PC 1 and PC 2.

The first two components account for 95% of the variation in PAH behaviour and appear to be related to the PAHs themselves.

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	9.02	86.7	86.7
2	0.823	7.9	94.6
3	0.164	1.6	96.2
4	0.116	1.1	97.3
5	8.11E-2	0.8	98.1

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Ace	0.089	0.040	-0.082	-0.222	0.134
Flu	0.073	-0.060	-0.192	-0.221	0.099
Phe	0.146	-0.061	-0.370	-0.162	0.018
Anth	0.098	0.010	-0.271	-0.028	0.099
Flanth	0.276	-0.052	-0.399	-0.119	-0.050
Pyr	0.260	-0.078	-0.444	-0.195	-0.148
Chr	0.280	0.003	-0.098	0.506	0.134
Banth	0.303	0.028	-0.168	0.554	0.277
Bflu	0.403	0.041	0.212	0.050	0.073
B(k)flu	0.325	0.033	0.254	-0.030	0.074
Bpyr	0.332	0.010	0.147	0.001	-0.205
Ind	0.332	-0.042	0.080	-0.134	-0.629
Bper	0.334	0.039	0.381	-0.096	-0.016
Dbanth	0.208	-0.050	0.171	-0.468	0.618
LOI	0.001	-0.011	0.022	-0.050	-0.007
TOC	0.015	0.986	-0.099	-0.080	-0.022
% Sand	0.004	-0.016	0.139	-0.013	-0.100
% Mud	0.003	0.007	0.095	-0.009	-0.043

7.10 Chapter Summary

The main grain size is in the sand fraction with the dominant magnetic mineral being magnetite. Correlations and PCA suggest a number of processes operating on this core including lithogenic controls on Si, Al, Ca, Zr, Ti, Sr, Ni, grain size factors on Ca and Mn, organic matter and diagenetic controls on Cd, Zn, Pb, As, Ni, V, Cu, Mn, Ca, Y, Ba, and pollution controls on PAHs, PCBs and a number of metals including As, Cd, Ni, Hg, Zn, and Pb.

The main pollutant metals show a general decrease in concentration towards the surface of the core, but as in the other cores there is very little obvious trend in the PCB or PAH data.

CHAPTER 8
UPPER MARSH CORE DISCUSSION

A number of parameters were measured for this core and they are discussed in this chapter. As the intention of this study was to investigate the historical pollution in the Liverpool area as recorded in sediment cores (in this case from the Mersey estuary), it was first necessary to eliminate factors other than pollution that could be responsible for the trends seen within the data. This was done by considering trends that could be explained by sediment composition, organic matter content and grain size effects before looking at data that could be explained by anthropogenic inputs.

8.1 The Influence of Sediment Composition in the Upper Marsh Core

The behaviour of several of the parameters measured in this core appears to be influenced to a certain extent by the sediment composition.

Si, Al, Ca, Zr show strong positive correlations with each other and with % very coarse silt. Si has a weaker positive correlation with Ti, % coarse silt, SIRM/ARM and SIRM, together with negative correlations with χARM/SIRM, χARM/χlf and % sand, suggesting that there is a mineralogical and maybe a grain size control on its presence (it appears to be related to the medium grain size fraction rather than the coarsest or finest fractions) (Hay *et al.*, 1997; Yang, 1997). These correlations suggest that Si, Ca and Zr are indicative of increasing mineral content and this is supported by the PCA scatterplot. Zr is also associated with minerogenic material which would explain its correlation with Si, and correlations between the two have been shown by Boyle (2001) to occur where silt mixes with other parts of the sediment. In order to confirm any grain size influence there would need to be a negative correlation with Ti and K which there is not, and this would indicate the relationship is due to the mineral composition of the sediment. Si (Fig 41) is the second most abundant element on earth. It is usually found in silicate or silica form as part of sedimentary rock – sandstone and mudstone are a major part of the geology of the region (De Vos *et al.*, 2005; BGS, 1997) – and any anthropogenic input into

the environment is usually masked out due to the naturally high background levels found (Aston, 1983).

The decrease in Ca concentration (Fig 41) at the top of the core could be due to decalcification taking place due to a lowering of the sediment pH caused by decomposition of organic matter (Luther and Church, 1988). Ca values show a decrease in the top part of the core (to 9cm) followed by a trend to increase with depth. This is similar to the trend exhibited by Si, particularly in the lower 25cm of the core. Ca is below ASV in the top part of the core but increases in concentration to above ASV from 10cm. Positive correlations with χlf (Fig 41), SIRM and Soft also indicate that its concentration is increasing with increasing mineral content (Maher, 1988; Dearing *et al.*, 1997), as does the weaker correlation it has with Zr, and the strong negative correlation with Br, which is often found associated with organic matter.

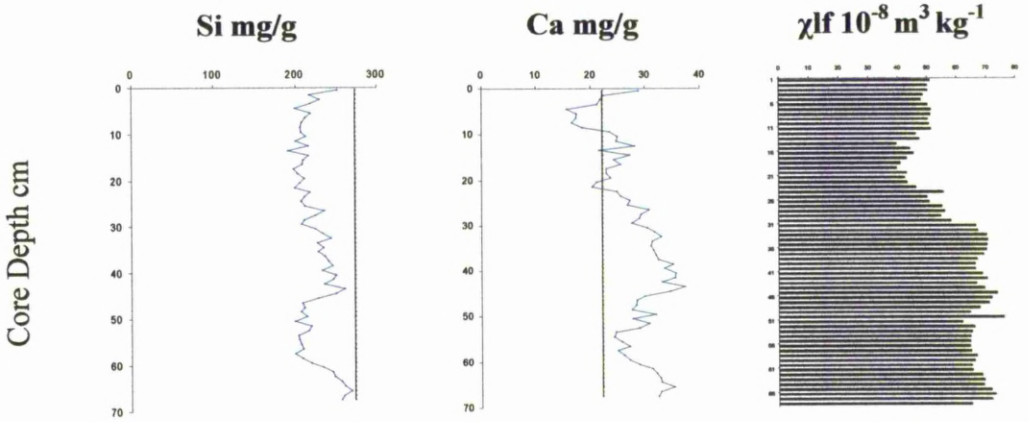


Figure: 41: Si, Ca and χlf.

The weak negative correlation Fe has with Si, Al, Ca, and Zr suggest that lithogenic input does not strongly influence its presence.

The positive correlations Ti shows with Si, Al, Ca, K, Zr and % very coarse sand suggest that it is probably present at natural background levels, has a lithogenic control on its presence and is higher in sediments with less organic matter present. It is a relatively resistant to weathering and has low mobility in the environment (Kabata-Pendias, 2007).

The weak positive relationship Sr has with Ca could indicate a calcareous rock or a shell material input to the sediment (Davidson *et al.*, 2005).

The weak negative correlation Ni has with Si, Ca, Al, and Zr would suggest that there is not a lithogenic control on its presence. However, it does show a weak positive with Hard % which could indicate a possible haematite/goethite link (Yang, 1997; Oldfield, 1994). Ni has weak negative correlations with χlf, SIRM and Soft. The magnetic relationship suggests that as the % magnetite in the sediment goes up the amount of nickel goes down.

The relatively stable concentrations of Al downcore indicate that it is present at natural background concentrations, as does the fact that it is below ASV. As Al is the most abundant metal in the lithosphere, its presence in sediment is usually related to the mineralology of the area rather than to pollution (De vos *et al.*, 2006). This is supported by the strong correlation it has with Si and the weaker ones it has with Ti, Ca and Zr – all of which have a strong lithogenic control on their presence.

8.2 Organic Matter Behaviour in the Upper Marsh Core

Both TOC and LOI values are low (TOC ~4%, LOI ~ 5-10%) (Fig 42) and show weak correlation with each other, indicating a small amount of organic matter is entering the sediment. Viguri *et al.* (2002) found weak correlations between LOI and TOC in sediments with low concentrations of organic matter. Changes in organic matter content (LOI) could reflect variation in the amount of productivity in the system (in years with a high level of productivity more organic matter will be deposited). They could also reflect a change in the terrestrial input to the sediment or, more likely, the establishment of vegetation as the saltmarsh develops. The higher concentration of organic matter could indicate a change in the aerobic conditions within the sediment core, possibly due to increased or decreased time the core spent submerged, due to changing flow conditions in the estuary as the main river channel moved position over time.

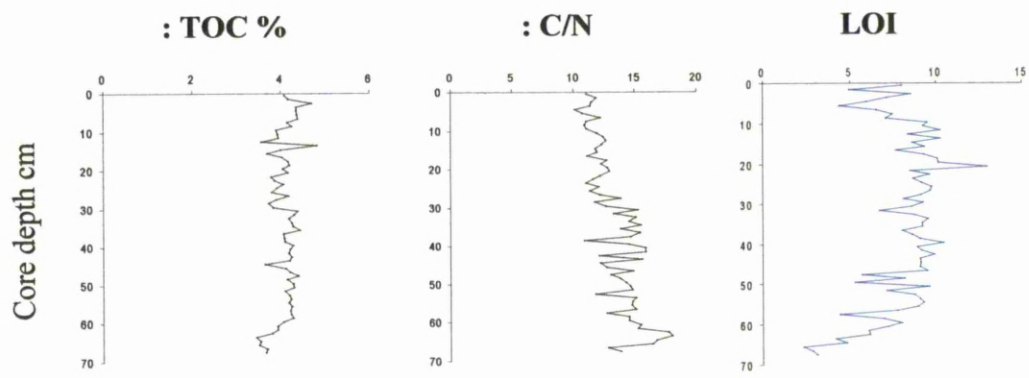


Figure 42: OrganicMatter Review.

The decrease towards the bottom of the core could be due to anaerobic bacterial degradation breaking down the organic matter to its constituent parts (Williams *et al.,* 1994). In anaerobic conditions the breakdown of organic matter will be slower. Variation in organic matter can also be related to the supply of nutrients to the estuary. In the upper part of the marsh the colonisation of the exposed sediment by vegetation such as *Spartina* species can lead to higher levels of organic matter as the mudflat develops into saltmarsh. The C/N ratio (Fig 42) indicates a mixed source of organic matter including both non-vascular aquatic plants (e.g. algae) and vascular land plants (e.g. plants from the surrounding saltmarsh area) (Meyers and Ishiwatari, 1993) which would be expected given the nature of the site's location. The increase in C/N ratio towards the base of the core suggests diagenetic remodification of the organic matter (Meyers and Ishiwatari, 1993; Pratono and Wolff, 1998) or it could be due to a change in the source of the organic matter. Values in the surface few centimetres are similar, if slightly higher, to those found during a survey of a transect on the opposite side of the estuary at Ince Marsh (C/N range 9.3 – 11.6) (Wilson *et al.*, 2005) and indicate a contribution from Particulate Organic Matter.

8.2.1 The Influence of Organic Matter on Element Trends

Previous work on the Mersey estuary has shown a positive correlation with trace metals and organic matter and fine grain sediments (silt fraction) (Rae and Aston 1981; Taylor, 1986; Harland *et al.,* 2000, Ridgway *et al.*, 2003).

LOI shows a weak negative correlation with Si, Ti, Zr which is probably due to these parameters being related to mineral matter content and this tends to be higher when organic matter content is lower. This is supported by a weak negative correlation with % very coarse sand. It is also negatively correlated with magnetic indicators of magnetic concentration in the mineral matter (χlf, SIRM, χARM, ARM) (Maher, 1988). It has positive correlations with Cl, Sr, Rb, Ni, and S whose concentrations are often related to the organic matter content in the sediment. It has a positive relationship with Hard % (an indicator of the haematite and goethite in a sample) (Yang, 1997) and a negative correlation with Soft which shows the percentage of magnetite in the sediment (Dearing *et al.*, 1997). The lack of strong correlations with metals could be due to the low levels of organic matter present or due to variation in the source of the organic matter (Luoma and Davies, 1983). At the surface of the core it is more likely to be related to saltmarsh plants, whilst deeper down the source could be marine algae.

Cl concentration (Fig 43) is well above ASV and, following an increase downcore in the first few centimetres, its values fluctuate to the bottom of the core. It shows weak positive correlations with Br (probably a seawater influence) and Fe, S, Rb and LOI. It has peaks at 24cm, 40cm and 52cm which correspond to peaks in S and could be due to the formation of Cl sulphide. These correlations are probably due to an association with organic matter and, possibly, the finer grain size fractions. This association is supported by negative correlations with factors that are influence by larger grain size and lithogenic controls (Ca, Zr, Al and Si). This relationship would suggest that the presence of Cl is related to natural input rather than an industrial pollution input.

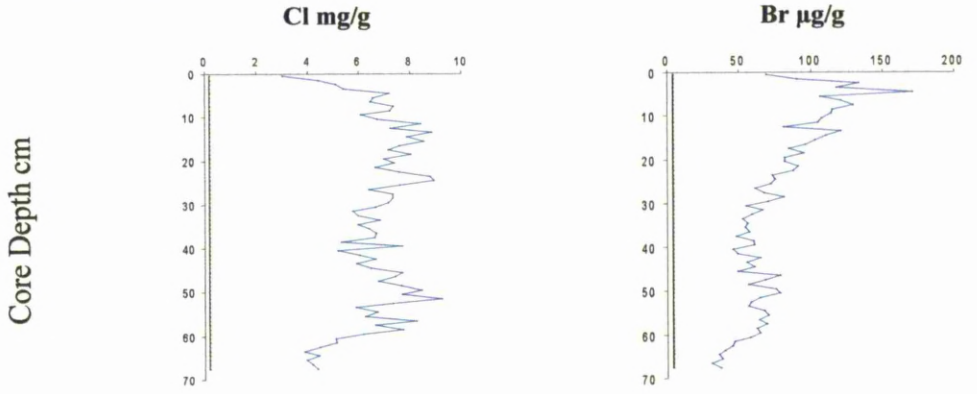


Figure 43: Cl and Br Profiles.

Br (Fig 43) is well above ASV and shows a downcore increase in the top part of the core followed by a decreasing concentration to the bottom of the core. Its profile is similar to that of Cl with which it shows a weak positive correlation. This is probably as these 2 elements are often associated in the marine environment due to a relationship with seawater. However, it also has a weak positive correlation with Fe, Mn, TOC and the coarse grain size fraction which could indicate an association with organic matter complexes in the coarse grain size fraction (Harvey, 1980). It has a negative correlation with finer grain sizes, the main pollutant metals and Si, Al, S and Ca. This would support the argument of a coarse grain size and organic matter control on its concentration and could suggest the presence of particulate organic matter. Br has negative correlations with parameters that indicate lithogenic controls on its behaviour (Si, Al, Ti, Zr).

Rb fluctuates downcore and is below ASV. It shows weak positive correlation with organic matter parameters (LOI, TOC) and other metals that have an organic matter relationship (Br, Cl). Sr values are low (below ASV) and seem to show a slight decrease downcore with the exception of a peak between 10 and 17cm. It has a weak positive correlation with S and LOI (0.01 level of significance) which suggests an organic matter control on its presence. Sr forms strong complexes with organic matter and clay mineral as well it forming metal sulphides.

8.2.2 The Influence of Organic Matter on Persistent Organic Pollutants Trends

The lack of strong correlations between organic matter and either PCBs or PAHs in this core could be due to the high levels of pollutant chemicals present and the low levels of organic matter, or the variety of sources of these chemicals. Boulou-bassi and Saliot (1993) stated that a lack of correlation with organic matter and PAHs was indicative of polluted sediments. PAHs generated by the burning of fossil fuels tend to be bound to soot particles generated at the same time and this limits their availability to bind with organic matter in the sediments (Pereira *et al.*, 1999).

The weak negative correlations between PCBs and organic matter (TOC and LOI) (and with magnetic indicators of grain size) are similar to what was found by Vane *et al.* (2003, 2007) and could be due to any relationship present being masked by the wide variety of sources of the PCBs. This disagrees with Camacho-Ibar and McEvoy

(1996) who found a positive correlation with organic matter and PCBs in the Mersey. Fox *et al.*, (2001) did not find a link between PCBs trend and organic matter in the Mersey.

8.3 Grain Size Effects in the Upper Marsh Core

The downcore change in grain size, as seen by the increase in the percentage of mud (Fig 44) could be an indicator of the change of depositional environment as the saltmarsh developed. The larger particles could be particulate organic matter deposited as the saltmarsh becomes vegetated. The high percentage of mud in the core is similar to that of a core taken in the vicinity by Ridgway *et al.* (2003). The increase in organic matter in the top of the sediment is likely to be due to the formation of saltmarsh plants as the marsh stabilised. This could lead to an apparent increase in metal values due to the association between metals and organic matter which could give a false impression of increasing pollution (Valette-Silver, 1993).

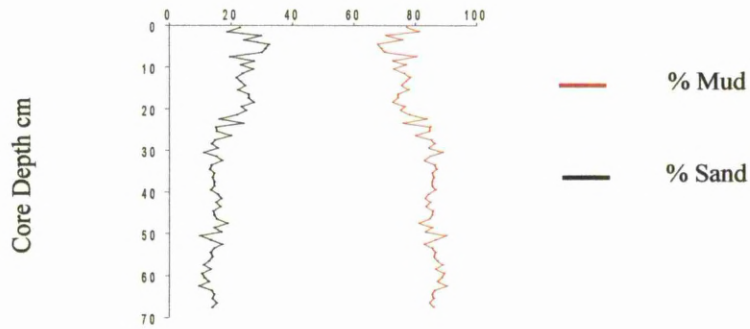


Figure 44: Grain Size Profile.

The concentration of Al is often related to the finer grain size fraction and it shows a weak positive correlation with these parameters (% very coarse silt, % mud and % coarse silt) and weak negative correlations with the large grain size fraction (% sand, % coarse sand, % medium sand and % fine sand) in this core (Velde *et al.*, 2003). The weak negative correlation it has with magnetic indicators of grain size (χARM/SIRM and χARM/χlf) also support this – as grain size decreases Al concentration increases (Camacho-Ibar, 1992).

The weak positive correlation that Si has with coarser silt and weak negative correlation with % sand would suggest that there is a weak grain size affect on its presence.

Zr is weakly negatively correlated with LOI, probably due to Zr content being related to coarser grained sediment and quartz (Fralick and Kronberg, 1997). The relationship to coarse grained sediment is supported by the positive correlations it shows with % coarse silt, % very coarse silt, Ca, Si and Ti, and the negative correlation it has with the finer grain size fractions and LOI.

It would appear that there is a grain size control on Fe (with the smaller grain size fraction) affecting its concentrations (weak positive correlation with χARM/χlf and χARM/SIRM and a weak negative correlation with SIRM/ARM). This grain size relationship (albeit magnetic grain size) is likely to be due to the Fe forming surface coatings on the smaller grain side particles (Luoma and Davies, 1983).

Ca has strong positive correlations with Si, χlf, SIRM, % very coarse silt and % coarse silt and weak positive ones with Al, Ti , Zr, Sr, HIRM, SIRM/ARM, -20mT and -30mT, as well as a strong negative one with % fine sand and weaker negative ones with χARM/SIRM and χARM/χlf. These correlations indicate a grain size control on its presence as well as a possible link to magnetic concentration (Thompson and Oldfield, 1986; Maher, 1988).

K shows a fairly steady downcore profile with a relatively small degree of fluctuation. It has a weak positive correlation with Ti, Fe, S, Cl and fine grain sediment as well the as slightly coarser % medium sand fraction and a weak negative one with Zr and mean grain size. Even though it is the eighth most abundant element (De Vos, 2006) it is often found in low concentrations because it is very important in plant physiology and usually preferential taken up by plants (BGS, 1997). The correlation with finer grained sediment is likely due to K forming clay mineral lattices which reduce its mobility within the sediment. It is below ASV and this indicates that it is probably present at natural background levels. K can be present in sediment due to a seawater influence as well as from lithogenic sources (Williams *et al.*, 1994).

S has weak positive correlations with the finer grain sizes (and weak negative ones with the coarse fractions) and magnetic concentration parameters and magnetic grain size parameters.

Nickel has weak positive correlations with % fine sand at the 0.05 level which could indicate a particle size a control on its presence. Pb, Zn, Hg and Cd all positively correlate with fines, suggesting a grain size relationship. Cr would also appear to have a weak positive correlation with the coarse grain size fractions and a weak negative one with fine grain size sediments. Harland *et al.* (2000) found a strong correlation between Hg and the silt fraction of the sediment, as did Campbell *et al.* (1986).

Rb shows weak positive correlation with the fine grain size fraction (% fine silt), and has negative correlations with coarser grain size (% very coarse silt) controls. Rb has a tendancy to bind strongly to clay minerals (BGS, 1997).

Sr values are low (below ASV) and seem to show a slight decrease downcore with the exception of a peak between 10cm and 17cm. It has a weak positive correlation with SIRM, Soft, and fines (0.05 significance level). These suggest a fine grain size control (or even a relationship to the magnetite concentration) on its presence which is supported by a weak negative correlation with coarser grain size fractions (Maher, 1988[b]; Dearing *et al.,* 1997).

Of the PAHs that show a grain size relationship, it would appear to be with the finer grains size fractions (positive correlations with % coarse silt and PCA data) and not with the coarse grain sizes (negative correlations with % sand). This agrees with the work of Vane *et al.* (2007) in the Mersey estuary, who found PAH concentrations to be higher in the muddy sediments than in the coarser sandy fraction. They suggested that this was due to the hydrophobic nature of PAH leading them to bond to organic matter which is often in higher concentrations in the finer grained sediment. This was not supported by a correlation with organic matter but this could be due to the relatively low levels present.

PCBs show negative correlations with the finer grain size fractions (and magnetic indicators of grain size) and positive ones with coarser grain size material. The association with coarse particles could be due to remobilisation of the PCBs in porewater as suggested by Brownawell and Farrington (1986). Fox *et al.* (2001) found no link between grain size and PCB contamination in their study.

8.4 Upper Marsh Core Magnetic Results Discussion

8.4.1 The Origin of Magnetic Particles in the Environment

There are a wide variety of sources for magnetic particles. The one this study is most concerned with is the human origin *via* pollution. Magnetic particles are generated by man through processes such as metal processing, rubbish incineration and the burning of fossil fuels (Flanders, 1994). However, these are not the only source and it is important to differentiate between manmade magnetic sources and those produced naturally, such as by the erosion of igneous rock and subsequent deposition and potential redeposition of the sediments generated. Magnetotactic bacteria create magnetite particles which they use for navigation and when the bacteria die these particles remain whilst the organic parts break down. Processes (both biological and chemical) that occur during soil formation (Maher, 1988) can also lead to the production of magnetic minerals.

A dilution of the detrital magnetic signal can be caused by diamagnetic enhancement due to the presence of authigenic minerals such as greigite (Snowball and Thompson, 1998) or bacterial activity producing magnetic minerals (Farina *et al*, 1990).

8.4.2 Upper Marsh Core Magnetic Properties

The positive correlation of χlf with Soft and a negative correlation with Hard % indicate that the dominant mineral is magnetite. This is supported by the high values of -300mT (Oldfield and Yu, 1994). Hard % increases slightly upcore and has a large peak between 16cm and 22cm, which suggests that the amount of haematite and goethite increases upcore relative to the magnetite which increases downcore (as illustrated by an increase in Soft downcore) (Dearing *et al.*, 1997; Yang, 1997). χlf also shows strong positive correlations with the finer grain size fractions (and negative ones with the coarser grain sizes). The increase in grain size ratios

downcore supports the grain size data which shows a slight increase in the percentage of mud downcore and a decrease in the percentage of sand. Zr also correlates positively with χlf and SIRM which could be indicative of a pollution input or it could be due to a grain size control operating on the metal. SIRM shows a strong positive correlation with Zn and Pb (and a weaker positive one with Hg and Cd) which has also been seen by Georgeaud *et al.* (1997). χlf and SIRM are also positively correlated with the fine grain size fraction of the sediment which could at least partially explain their relationship with the metals, as these metals are also correlated with the fine grain size fractions.

%FD values are low, which would suggest that the bulk of the magnetic signal is from non-soil sources (Thompson and Oldfied, 1985; Scoullos and Oldfield, 1986). This is due to the fact that the FD% is derived from weathered soils and represents fine grained magnetic crystal that are only present in very small amounts in anthropogenically derived materials.

It is possible that the peak in magnetic parameters χARM/SIRM, χARM and χARM/χlf could be somehow related to the peak in S at around 29cm. If this relationship is deemed to be true then it is possible that these magnetic parameters have the potential to be used to identify the location of the sulphide reducing zone and, hence, could be powerful aids in identifying diagenetic processes within sediment. However, they do not show a corresponding relationship with the peak in S at 50cm which indicates that the relationship is indicating a link between χARM and the metal pollution in association with S.

8.5 The behaviour of Elements and Persistent Organic Pollutants in the Upper Marsh Core

The peaks in Mn (Fig 45) and, to a lesser extent, Fe (Fig45) in the top layers of this core could be due to diagenetic remobilisation of these elements. The sediments in the lower part of the core could have become anoxic, which can lead to the solubilisation and then remobilisation of these metals and eventual redeposition higher up the core (Spencer, 2003). This process can lead to an increase in

contaminants in the sediment surface layers which could be misinterpreted as an increase in pollution input when, in fact, it is due to redistribution of metals already in the sediment (Valette-Silver, 1993). High Mn in the surface layers could be due to formation of Mn oxyhydroxides in oxic conditions (O'Reilly Weise *et al.,* 1995). The lack of a positive correlation with Ti and K support the idea that Fe and Mn presence is related to diagenesis and not to a grain size influence. The peak in Mn is also associated with a peak in Br which suggests that the Br concentration maybe related to Mn and, therefore, is controlled by the diagenesis of the Fe/Mn oxyhydroxides in association with organic matter, rather than by any lithogenic influences. From the correlations, it would appear that Mn distribution within the sediment is associated with a range of grain sizes, which supports the argument that its presence is related more to diagenetic processes than a grain size effect. The fact that concentrations are around ASV indicate that there is not anthropogenic enrichment of Mn in the sediment and that the large peak at 10cm is related to diagnetic remobilisation, rather than pollution.

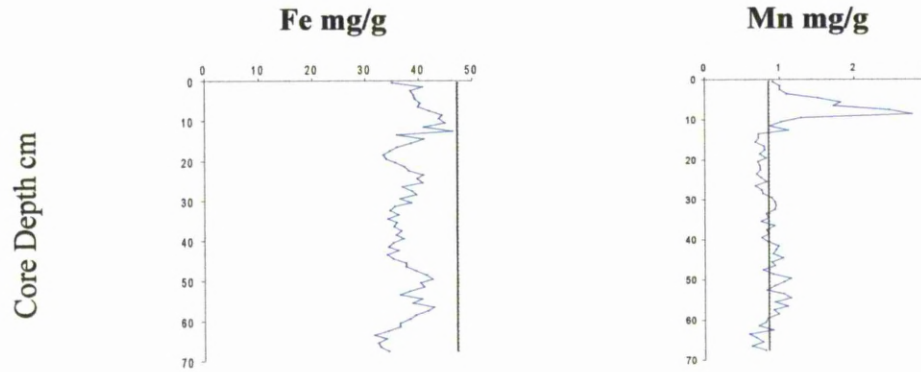


Figure 45: Fe and Mn Profiles.

The peak in Fe at 10cm depth is followed by a decrease in concentration which could mean that there has been some post-depositional remobilisation from lower down the core (Cundy and Croudace, 1995). Redox potential is one of the most important factors in the way metals behave in sediments, and is dependent on the depth to which the sediments are oxic. This can be affected by the amount and frequency of water-logging in the sediment or saltmarsh, so areas that are more likely to be submerged will have less chance of being oxic and larger grain sizes will allow the sediment to drain more quickly and therefore allow more oxygen penetration (Jones and Turki, 1997). As this core was taken from high up on the saltmarsh it would be

exposed to air for the majority of the time. The increase in Fe with depth in the surface layers could be due to it being trapped by authigenic carbon/sulphide formation (Cundy and Croudace, 1995). Fe correlates positively with Mn reinforcing the conclusion that there is a diagenetic control on its behaviour.

As mentioned earlier there does not appear to be a lithogenic control on the behaviour of Fe, but there is a grain size influence likely to be due to the Fe forming surface coatings on the smaller grain size particles ((Luoma and Davies, 1983). Concentrations of both Fe and Mn are of similar orders of magnitude as those found by Langston (1986). The weak positive correlation Fe shows with Cl and Br could indicate a marine influence on its behaviour, or this could just be due to grain size and diagenetic controls on these metals. It does not correlate with any of the indicators of pollution input so its presence is probably not due to an industrial input to the sediment and this would also suggest the pollutants concentrations has been influence too much by diagenetic remobilisation. The Merseyside area has low background levels of Fe and, other than diagenetic remobilisation, any peaks can usually be related to industrial contamination (BGS, 1997). Due to the low levels Fe exhibits and the correlation it shows with Mn, it is probable that the peak in the surface is not related to pollution but to diagenesis. However, Turner (2000) found no correlations between trace metals in Mersey sediments and Fe or Mn and explained this was due to the dispersal of fine sediments by strong currents having a buffering effect on localised metal levels.

Nickel fluctuates above and below ASV downcore and has weak positive correlations with Br (at the 0.01 level) and Cl (at the 0.05 level). The weak relationship with Cl could be an indication that Ni is forming chloride compounds. It also has a weak negative correlations with Cd. Ni can be related to fuel combustion, but the weak negative relationship it has with total PAHs does not support this as a source in this case. The fact that it fluctuates above ASV in places suggests that there is an anthropogenic input to the sediment, as background levels in the region are low (BGS, 1997). Sources of nickel to the Mersey include a catalyst manufacturer (which ceased production in 1989, replacing it with Ni oxide on alumina substrate until 1998) and a number of edible oils factories that use it as a catalyst (Martino *et al.*,

2004), with the main source at present being thought to be remobilisation from tidally resuspended contaminate sediment (Martino *et al.*, 2002; 2004).

Al has a low mobility in sediment, which would account for the weak negative correlation with diagenetic indicator elements such as Fe and Mn (Shiller and Frilot, 1996). The weak correlation with metals Zn and Cd could be an indicator of a small anthropogenic input from sources such as smelting, cement manufacture, sewage and dust (Reimann and de Caritat, 1998).

Si is below ASV (probably because shale itself tends to be very fine grained and have low values of Si) and shows a fairly steady downcore trend with a relatively small increase. There is a drop in concentration between 47cm and 60cm depth. Si concentration can also be due to biological activity within the water column or sediment. Various organisms (e.g. diatoms) have silica as part of their bodies and when they die this silica is released back into the water column or sediment (Coleman and Bratton, 2003).

The peaks in Ca downcore could be related to pollution input or agricultural activity in the regions. Anthropogenic sources of Ca include cement factories and fertilisers (BGS, 1997; Reimann and de Caritat, 1998). The increase downcore could also be related to a seawater input (Ogichi *et al.*, 2000), with the lower core being from a time when the marsh was lower and therefore spent more time submerged by the tide, which lead to higher levels of Ca being deposited in the sediment. In general, anthropogenic influences on Ca are insignificant due to high lithogenic inputs into the environment, but there is a weak correlation with Pb, Zn, Cd and Hg which could indicate an anthropogenic element to the Ca concentrations, as could the weak positive correlation with S (which can be release from Cu smelting (de Vos *et al.*, 2006). The weak negative correlation Ca has with Mn suggests a redox control on its presence, with Mn being remobilised under anoxic conditions and $CaCO_3$ likely to precipitate out in seawater (Hylander *et al.*, 2000). Higher than ASV levels can be related to the nature of the bedrock in the surrounding regions (the Irish Sea till and coastal aeolian sands – which have high levels – and other local anomalies), but anthropogenic contamination can occur from cement and concrete usage in a local

area (BGS, 1997). The weak positive correlation Ca shows with Sr is probably due to a shared source from the shells of marine organisms (Ridgeway *et al.*, 2003).

There is a gradual increase in S with depth and there are two large peaks in concentration. S often shows a large increase just above the sulphate reduction zone, so it is possible that these indicate the location of this zone (Rae, 1997). There also appear to be peaks in Zn and Cl associated with the lower S peak and a Pb peak associated with the higher one. These could indicate the precipitation of insoluble metal sulphides (McCaffrey and Thomson, 1980; Zwolsmann *et al.*, 1993). S has a weak correlation (and a similar distribution on the PCA scatterplot) with Pb and Zn, possibly indicating a post-depositional or subtle organic control on their relationship.

Apart from the very top of the core, S concentrations are above ASV. It has weak positive correlations with Ca, K, Cl, Cu Pb, Sr, Zn, Cd and Hg. The correlations with metals support the theory of the formation of insoluble metal sulphides (Cundy *et al.*, 2003) and suggest the possibility of a pollution input to the sediment. Sulphides can enter the aquatic environment from a variety of sources; including sulphuric acid using industries, coal combustion, smelting and mining (which could account for the relationship with Pb and Zn, as both these metals are often mined as sulphide forms), paper mills, tanneries, fertiliser usages and pesticide production (Alloway, 1995). However, the association could also be due to diagenetic remobilisation, although there are no obvious metal peaks associated with the major sulphur peaks, which would suggest that even if there is a diagenetic relationship, it is weak at best and cannot be used as an explanation for the downcore metal distribution (Lee and Cundy, 2001). If this was the case it would call into question the reliability of using Pb and Zn as a method of dating this core (Cundy *et al.*, 2003).

Cr values fluctuate wildly, which could be due to a sensitivity issue with the XRF, in which case the correlations it shows are likely to have occurred by co-incidence and not be a true representation of it behaviour. However, if this is not the case the weak positive correlation it shows with Fe and Cl could be due to a diagenetic remobilisation control on its presence and Cr has been shown to associate with Fe (Turner, 2000; Hursthouse *et al.*, 2003). Chromite (an industrial source of Cr contamination) could be the reason for the above ASV levels of Cr in the Mersey or

it could come from the tinplating industry (Bryan and Langston, 1992). Cr also appears to have a weak negative one with certain PCBs (18, 49 and 141). Abu-saba and Flegal (1995) and Coomber *et al.* (1995) have shown that lower salinities favour the release of Cr from the sediment to the water column and this could explain why there are lower values at the top of the core and why it fluctuates wildy downcore – different inundations of the saltmarsh with fresh, brackish or seawater over time could have led to different levels of retention of Cr within the saltmarsh.

Natural background Pb levels in the region are low; therefore the high concentrations found in the sediment have to be related to anthropogenic activity (BGS, 1997). Zn, Pb, Hg and Cd (Fig 46) concentrations are of similar orders of magnitude as those found by Langston (1986). The downcore profiles of those metals that have a potential pollution origin (Cd, Hg, Zn and Pb) are all similar. They show an increasing concentration towards the bottom of the core. This is similar to the trend found with Zn and Pb by Fox *et al.* (1999). They are all present at concentrations above ASV indicating a pollution source. Cd is fairly close to ASV at the very top of the core however. The increase in Cd, Hg, Zn and Pb with depth is probably due to enrichment during historic anthropogenic input. As discharge regulations were tightened, the levels emitted to the environment reduced so those recorded in the more recent sediments are at a lower level than they were in previous years. Zn, Pb, Cd and Hg all positively correlate with each other and Zn, Pb and Hg plot along the same lines on the PCA scatter plot, indicating there is a pollution input control on their presence. Cd often occurs as a substitution element in Pb, Zn, Hg and Cu sulphides (BGS, 1997).

Pb, Zn, Hg and Cd all positively correlate with fines, suggesting a grain size relationship as mentioned previously, however correlations with other metals indicate a pollution control on their presence. Pb has a strong positive correlation with Zn, χlf and SIRM, which indicate that Pb and Zn are related due to pollution input to the system rather than natural background processes. The positive correlations these metals have with a number of magnetic concentration parameters (χlf, χARM, HIRM and SIRM) indicate that these magnetic parameters are potentially good indicators of increasing metal contamination in sediment (Scoullos *et al.*, 1979; Oldfield and Scoullos, 1984; Beckwith *et al.*, 1986; Scoullos and

Oldfield, 1986; Oldfield, 1990). The downcore profiles of χlf and SIRM (and to a lesser extent χARM and Soft) seem to match those of Pb and Zn and both these metals shows positive correlations with χlf (strong with Zn and weaker with Pb) as do other potential 'pollution' metals such as Sr, Hg and Cd. This suggests that in this core χlf would be a suitable proxy to use to predict heavy metal pollution as would SIRM (Berry and Plater, 1998; Rubio *et al.*, 2001). Their lack of correlation with Mn (except for Cd) and Fe would suggest they have not been subjected to post depositional remobilisation, which could be due to them forming insoluble metal sulphides and this is supported by a weak positive correlation with S (McCaffrey and Thomson, 1980). The relationship with S could also be due to pollution influence, as copper smelting often releases SO_2. There is also a possibility of a mining input to the sediment with both Pb and Zn sulphides have been mined locally (Fox *et al.*, 1999; Harland *et al.*, 2000).

Turner (2000) concluded that lower levels of Pb compared to Zn in the Mersey were due to the differences in transport modes bringing them into an estuary. He concluded that atmospheric sources were the more important source for Pb whereas an aquatic input was important for Zn.

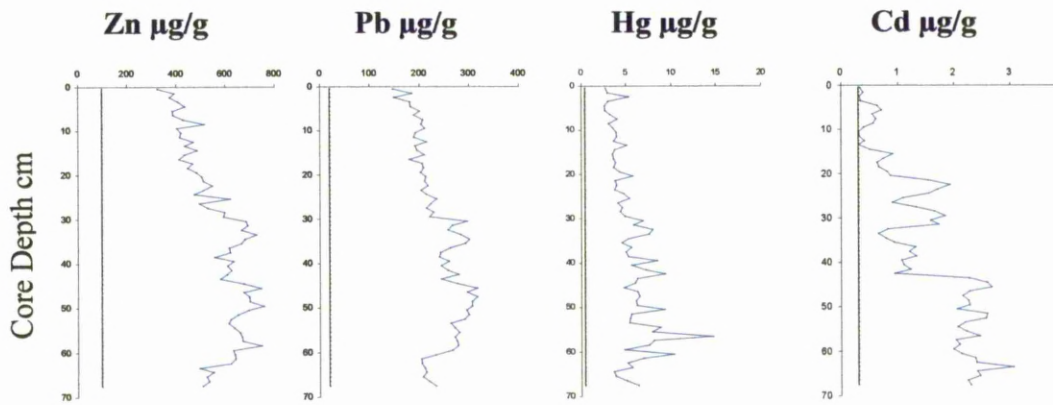


Figure 46: Zn, Pb, Hg, Cd Profile.s

Both Pb and Zn show an increase with depth to 60cm where there appears to be a slight drop in concentration. This could be showing that the historic pollution levels have peaked and that the decrease in metal values below 60cm can be related to the changes in historical discharges. The increase in Pb from 60cm to 45cm could be mirroring the increase in industry and in particular the use of leaded petrol in motor

vehicles in the 1950s, in which case it could be a good marker to use to help date the core. This trend has been documented by other authors (Cundy *et al.*, 1997; Harland *et al.,* 2000) and values fall within the ranges found by these authors. The decrease in concentration of Pb and Zn between 45cm and 37cm could be related to sediment input to the area. For example if, for some reason, there was an increase in sedimentation rate, then the levels of Pb and Zn might have appeared to drop, when in actual fact all that had happened was their values had been diluted over longer core section. There does appear to be a peak in Zn in the top 10cm associated with a peak in Mn, which could indicate that there has been some diagenetic enrichment at that depth which would mean that the peak in Zn is not associated with a pollution input but with diagnosis and should not be attributed to pollution.

Cd shows a greater fluctuation downcore than the other metals and a weak association with Mn which could be due to it co-precipitating with Mn oxides. Cd can volatilize at high temperature and enter the atmosphere e.g. from incineration. This could point to an atmospheric deposition source for it in the sediment. Cd has been shown to be much more easily remobilised from sediments than many of the other heavy metals, which could account for its positive correlation with Mn (Giblin *et al.*, 1980).

Hg concentrations decline towards the top of the core in recent years and correspond to levels found by in the Mersey by Rae and Aston (1981), Fox *et al.* (1999), Harland *et al.* (2000) and Vane *et al.* (2009) and also by Mirlean *et al.* (2001) from domestic effluent from Rio Grande which itself corresponds to levels found in other polluted estuaries. Historic levels found on suspended matter in the Mersey have been around 10μg/g and historic measurements of mercury in sediment have found levels of between 3μg/g and 20μg/g (Airey and Jones, 1982). The correlation Hg has with S could indicate the formation of sulphide complexes (Lu, 1986). The decline in Hg values from 35cm depth towards the top of the core could correspond to the introduction by ICI at Runcorn (one of the two main sources of chlorine production in the region – and, therefore, Hg releases to the Mersey) in 1974 of a major effluent treatment plant (Harland *et al.,* 2000). This plant reduced discharged from ICI from 60 tonnes of Hg per year to less than 0.5t per year by 2000 (Harland *et al.*, 2000).

It should be noted that, although Hg input to the Mersey has fallen by around two orders of magnitude, the corresponding levels in the sediment have not fallen by anywhere near as much. This could be due to the fact that discharges are not made directly to the Mersey, but to tributaries such as the Weaver and the Manchester Ship Canal (Langston, 1986), where it is likely they are deposited initially and resuspended at a later date by the dredging operations that occur in these locations, which would also explain the various spikes in Hg concentrations seen downcore (Harland *et al.*, 2000; Vane *et al.*, 2009). The other reason could be that the finer sediment fraction in the Mersey has a tendency to remain within the estuary for long periods of time before eventually being removed to the Irish sea (Murdock *et al.*, 1995) therefore, the estuary is actually accreting sediment and the retention time within the estuary for pollutants associated with that sediment is likely to be decades. The peak in Hg concentration at 12cm depth could be related to the erosion of the saltmarsh north of Ince and Stanlow that was seen to occur around this time, which could have led to redistribution and redeposition of any stored pollutants to other areas of the marsh (Harland *et al.*, 2000). There are associated peaks in other pollutant metals (Pb, Zn) around the same depth. The lack of any correlations with organic matter indicates that Hg concentrations in the core are related to usage rather than to a link with organic matter but levels of organic matter in the sediment are low which could also explain the lack of correlations. This finding is in conflict with that of Vane *et al.* (2009). In this study several metal levels (Cd, Cr, Pb, Hg) were higher than those recorded by Harland *et al.* (2000) whilst Zn was of similar levels. The trend of decreasing concentration in recent years was the same however. Ridgway *et al.* (2003) found the highest levels of contaminations around 30cm and this also corresponds with the maximum found in this study at around 50cm depth.

Hg, Zn and Pb exhibit weak negative correlations with a number of PCBs which could be due to a grain size influence and it could also suggest differing pollution inputs of the chemicals. Profiles of these metals appear to conform somewhat to the data generated by Fox *et al.* (1999) from Ince Marsh and would indicate that the peak in Pb and Zn at 50cm could correspond to the peak in this core in 1950 and the peak at 35cm depth would correspond to the peak in the Fox *et al.* (1999) data around the mid 1970s.

Zr shows weak positive correlations with PAHs which could indicate a pollution control on its presence (Zr can be released from brake pads).

The decline in pollution metals towards the surface of sediment from the Mersey has been shown by Harland *et al.* (2000) for Zn, Pb, Cr, Cd and Cu. The downcore metal profiles also compare well with a core taken for a Master's Thesis (Mills, unpublished). Comparison with this thesis and the work of Fox *et al. (1999)* would lead to the conclusion that the core represents approximately 60-70 years of sediment accumulation approximately dating back to the mid 1930s. This is supported by the presences of PCBs at the base of the core, if the core was pre-1930s then it would be expected that there would be no PCBs present. The dating would also suggest an approximate sedimentation rate of ~1cm per year. However, it is likely that in the top part of the core this has slowed down due to the formation of more stable saltmarsh, meaning that the top part of the core is only subject to submersion on the highest tides, so the amount of sediment brought onto the location is reduced.

8.6 PCBs in the Upper Marsh Core

PCBs and PAH are present in the environment due to anthropogenic processes. PCB concentrations fluctuate markedly downcore, but there appear to be several coincident major peaks in the concentration of most congeners at 7cm, 12cm, 23cm, 47cm, 53cm, and 64cm. PCB 66 does not appear to have these peaks. Fox *et al.* (2001) found a increase in PCB concentration down core which was not reflected in the wide variations seen in this core. Concentrations appear to be lower than those found by Fox *et al.* (2001) at Widnes Warth and do not reflect the large maximum peak found at around 15cm. The lack of any real trend is probably related to the variety of sources of PCBs in the region and to their persistence within the environment (Vane *et al.*, 2003). Both these factors mean that there is a constantly changing input to the system from a number of sources including legitimate industrial release, leaching from landfill, accidental releases and remobilisation from other sediment stores due to anthropogenic (e.g. building work) or natural (storm events) disturbances. The majority of PCBs appear to correlate well (if weakly) with each other (PCB 66 shows the fewest correlations) and this is also likely to be related

to the mixed sources of these chemicals. There appears to be a general trend of lower values and a slightly more stable profile in the mid part of the core (between ~25 and 40cm). If we consider the core dating proposed using the Pb data, this period would correspond to the mid 1970s, a time when the dangers of PCBs became apparent and stricter discharge regulations were introduced. The increase upcore following this more stable period could be due to the same factors mentioned above as, even though general releases to the environment were being more strictly controlled, accidental releases, leaching and sediment resuspension were still occurring. Plus, in recent years there will have been an increase in the decommissioning of industrial equipment containing PCBs and an associated release to the environment of some of these PCBs (Fox *et al.*, 2001). The large peaks in several congeners at various points in the core could be related to accidental discharges that may have occurred in the vicinity over the years, or to large scale remobilisation of sediment stores during storm events.

The presence of PCBs at the bottom of the core indicates that the core depth has not reached pre-PCB production depth so, therefore, does not go back further than the 1930s or 1940s, which would support the proposed time line suggested in the metals section above.

Vane *et al.* (2003) found the dominant PCB homologue groups to be tri, tetra and penta chlorinated congeners, Fox *et al.* (2001) found the dominant congeners to be penta and hexa chlorinated, whilst this study showed the dominant groups to be tetra and hexa chlorinated congeners with the other homologue groups showing a variation in relative importance downcore. This relatively consistent downcore trend does not support the findings of Alcock *et al.* (1993) that there was a change in the relative proportions of the homologues downcore due to a process of volatalisation and remobilisation of the lower chlorinated congeners. Vane *et al.* (2003) suggested that this was due to estuarine sediment only being exposed to the air for relatively short periods each day. In this core there does not appear to be any bacterial reduction of the PCBs occurring as was found by Borja *et al.* (2005). It is possible that the concentration of PCBs are too low for dechlorination to occur (Sokal *et al.*, 1995) or that co-contamination limits dechlorination from occurring (Sokal *et al.*, 1994; Zwiernik *et al.*, 1999).

Of all the PCBs investigated PCB 66 shows the fewest correlations with other PCB (and all that it shows are weak). It is possible this is because PCB 66 can co-elute with PCB 95 which could be confusing the correlations. All PCBs apart from PCB 28 and 66 show a negative correlation with Hg. Several are also negative with Zn, Pb, Sr, or S. PCB 49 has negative correlations with Cr, PCBs 138 and 194 have a negative correlation with K, PCB 156 has a negative correlation with K and Mn. The only PCBs that show positive relationships with the metals are PCB 47 and 194 (Br), PCB 66 (S and Cd), PCB 170 (Y). PCB 18 shows a weak positive correlation with Acenapthene and PCB 66 shows a weak positive one with Phenanthrene, There are several PAHs that show weak negative correlation with PCBs: benzo[b]fluoranthene, chrysene, total PAH, benzo[a]anthracene and benzo[k]fluoranthene.

Total PCB concentrations agree with levels found by Thompson *et al.* (1996) in the Mersey estuary at a location close to where this core was taken. Thompson *et al.* (1996) also found a correlation with fine grain sizes and the coarser fraction indicating as above that PCB are not necessarily relate to the fine grain sizes only.

8.7 PAHs in the Upper Marsh Core

8.7.1 PAH Concentrations

PAH concentrations fluctuated throughout the core and this is indicative of the wide variety of sources of these compounds leading to the lack of any observed trend in their distribution through the core. As with the PCB data, PAH concentrations fluctuate markedly downcore with several coincident peaks in concentration occurring at 23cm, 30cm, 35cm, 48cm, 52cm and 63cm. The peak at 30 cm seems to be particularly obvious when compared to the others. Chrysene concentrations seem lower in the top part of the core with several peaks in concentration occurring between 48cm and 63cm depth. PAHs show good positive correlations amongst themselves and with the PCBs mentioned above. There appears to be an increase in many of the PAHs from ~40cm depth to ~25cm depth. It is possible this is related to the increased industrialisation of the area in the 1950s and 1960s and also the increase usage of motor vehicles during this time. The general trend from 25cm

depth towards the top of the core appears to be an overall decrease in concentrations (although values do fluctuate and this could be related to stricter industrial discharge regulations, the reduction in the use of coal for residential use and cleaner technologies being introduced in motor vehicles.

There are several metals that show positive correlations with PAHs: Cr (acenapthene) Zr, (fluorene, pyrene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[a]pyrene), Zn (fluorene), Ca (phenanthrene), Hg, (phenanthrene), S (phenanthrene, chrysene), Cd (chrysene) and several that show negative ones Cd (benzo[ghi]perylene), Br, (chrysene fluoranthene) and pyrene is negative with LOI. Hg is often emitted from coal fired power plants which could explain its correlation with PAHs (Valette-Silver, 1993), as could the relationship with Zn and Pb and Cu. Aside from fluorene and phenanthrene which have weak positive correlations with χlf, the lack of correlations with the magnetics data could be related to the mixed sources of the PAHs (see PAH ratios discussed below). Positive relationships between PAHs and magnetics data have been attributed to the source of the PAHs being fly ash from coal fired power plant (Morris *et al.*, 1994). However, if this source is mixed with a petrol and diesel source it could prevent any positive relationships being noted. This would mean that in a core with mixed sources of PAHs χlf is not necessarily a good indicator of PAH contamination.

If the source of PAH is pyrolitic, positive correlations with organic matter would be expected, but there are none (Vane *et al.*, 2007). Pyrene actually shows a weak negative correlation with LOI. This could be for the same reason as the lack of organic matter correlations shown by PCBs, i.e. the varied source of PAHs (Vane *et al.*, 2003) but it could also be due to the fairly low levels of organic matter found in this sediment and the high levels of PAHs, i.e. there is not enough organic matter present for the PAHs to adsorb to. Another potential reason for the negative correlations is that the source of PAHs could be petrogenic rather than pyrolytic.

High levels of PAHs (11μg/g) where also found by Rogers *et al.* (2002) at a sampling site in the vicinity.

When looking at the downcore distribution of individual PAHs, it can be seen that for all depths benzo[b]fluoranthene dominates. In the top 30cm of the core the higher molecular weight PAHs can be seen to be present in higher concentrations than the lower molecular weight fraction and this corresponds to work done by Rogers (2002), who suggested low molecular weight PAHs are more likely to be remobilised from sediment and be more bioavailable. However, towards the bottom of the core, this distribution is less obvious (in all core sections the lowest molecular weight PAHs – acenaphthene and fluorene – contribute the smallest amount to the total concentration).

The same nine pyrolytic species as found by Vane *et al.* (2007) were dominant all though the core (Flan, Pyr, Chr, BaA, BbF, BkB, BaP, I1,2,3,P and BghiP) but there is some variation between each sample depth. This is likely to be due to the variety of sources of PAHs to the estuary (including chemical plants, oil refineries, sewage works, power stations and the docks).and the physical disturbance caused by the tidal mixing leading to resuspension and redistribution of the sediments (and their associated contaminants) on a regular basis (Rogers, 2002; Vane *et al.*, 2007). The dominance of the higher molecular weight PAHs could indicate a high temperature combustion source (such as incineration) or it could be due to the higher molecular weight PAHs being preferentially adsorbed onto particulate matter and incorporated into the sediment (Witt, 1995). Lower concentrations of the lower molecular weight PAHs could be explained by the fact that they have a tendency to be found in the vapor phase (Guo *et al.*, 2003; Cailleud *et al.*, 2007).

Due to the large number of sources of PAHs to the Mersey estuary (Readman *et al.*, 1986) it can be incredibly difficult to identify a particular pollution event such as an oil spill. This was discovered by Davies and Wolff (1990) during their investigation of hydrocarbons following an oil spill in 1989. They found that the high background levels of pollution in the sediments all but masked out the input from the spill.

Readman and Mantoura (1987) found that PAHs from a combustion source are not subject to major decomposition in anaerobic sediment therefore concentrations found should be representative of historical inputs.

8.7.2 PAH Ratios

PAH ratios (Table 4) have been used by many authors (Grimmer *et al.*, 1983; Prahl *et al.*, 1984; Takada *et al.*, 1990; Rogge *et al.*, 1993a,b; Khalili *et al.*, 1995; Gogou *et al.*, 1996; Neilson, 1998; Caricchia *et al.*, 1999; Pandey *et al.*, 1999; Kavouras *et al.*, 2001; Oda *et al.*, 2001; Mandalakis *et al.*, 2002; Park *et al.*, 2002; Guo *et al.*, 2003 Fang *et al.*, 2004; Mantis *et al.*, 2005; Ravindra *et al.*, 2006a, 2008) as a method of identifying the source of the PAHs found. Their use assumes that those being compared are diluted to the same extent during transport from the source and during dispersal in the environment.

PAH Diagnostic Ratio	Source	Value	References
Fluoranthene/pyrene	Vehicular	0.6	Neilson (1998)
Pyrene/B[a]P	Diesel engine	~10	Oda *et al.* (2001)
	Gasoline engine	~1	
CPAHs/TPAHsa	Combustion	~1	Prahl *et al.* (1984); Takada *et al.* (1990); Mantis *et al.* (2005) Ravindra *et al.* (2006a, 2008); Gogou *et al.* (1996)
Indeno[1,2,3-cd)pyrene/benzo[ghi]perylene	Gasoline	< 0.4	Caricchia *et al.* (1999)
B[a]P/benzo[ghi]perylene	Traffic emissions	0.5	Pandey *et al.* (1999); Park *et al.* (2002);
	Brown coal	>1.25	Pandey *et al.* (1999)
Benzo[b]fluoranthene/ benzo[k]fluoranthene	Diesel	>0.5	Pandey *et al.* (1999); Park *et al.* (2002)
B[a]P/(B[a]P+chrysene)	Diesel	0.5	Khalili *et al.* (1995); Guo *et al.* (2003)
	Gasoline	0.73	
Fluorene/(fluorene+pyrene)	Diesel	>0.5	Rogge *et al.* (1993a ,b); Mandalakis *et al.* (2002); Fang *et al.* (2004); Ravindra *et al.* (2006a, b)
	Gasoline	<0.5	
Indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd)pyrene+benzo[ghi]perylene)	Cars	0.18	Grimmer *et al.* (1983); Ravindra et al. (2006a, b) Kavouras *et al.* (2001)
	Diesel	0.37	
	Coal	0.56	
	Wood burning	0.62	
	Diesel emissions	0.35-0.70	

Table 4: PAH ratios used by other authors.

The PAH ratios found in this core indicate a variety of input sources including a mixture of diesel (benzo[b]fluoranthene/benzo[k]fluoranthene) and coal, as indicated by the indeno[1,2,3-cd]pyrene/ indeno[1,2,3-cd]pyrene+ benzo[ghi]perylene ratio, gasoline (fluorene/fluorene+pyrene, pyrene/benzo[a]pyrene, indeno[1,2,3-cd]pyrene/benzo[ghi]perylene and combustion. This supports the reasoning that the lack of correlations between PAHs and other pollutants is likely due to the wide variety of sources (road traffic, industrial combustion and power stations). Vane *et al.* (2007) found a mix of sources for PAHs in the Mersey

One interesting observation is that the concentrations of pollutant metals are decreasing towards the surface of the core whilst those of PAHs are not. This could be due to differing input sources (industry or atmospheric versus aquatic) or it could be due to differing behaviour of the pollutants once they have been deposited, with the metals being subjected to diagenesis and remobilisation and the organic pollutants being less influence by these processes.

8.8 Chapter Summary

As it can be seen from the complexity of the data, explaining the behaviour of metals and POPs in the sediment can be complicated, with multiple influences (grain size, lithogenic, organic matter and pollution) being potentially responsible for trends. The non-pollution related parameters were considered first to try to eliminate those metals whose behaviour could be explained by natural processes within the environment. Once this was done it became apparent that a number of metals are present due to pollution input (even though there are also natural controls – organic matter, grain size – operating on their behaviour).

The dominant magnetic mineral appears to be magnetite with an increase in the haematite/goethite content towards the surface of the core. Lithogenic factors appear to control the behaviour and concentration of a number of metals (Si, Al, Ca, Zr, Ti, Sr and Ni), whilst the organic matter content of the sediment has an influence on others (Cl, Sr, Rb, Ni, S and Br). The lack of a significant organic matter relationship

with PAHs and PCBs could be due to the relatively low levels of organic matter found in this core.

The sediment grain size is predominantly mud and the effects of grain size appear to be important on the behaviour of a variety of parameters (Si, Cl, Br, Al, Zr, Fe, Ca, K, S, Ni, Pb, Zn, Hg, Cd, Rb, Sr, PAHs and PCBs). Several elements have a diagenetic control acting upon them (Fe, Mn, Br, Cl, Si, Pb, Zn and Cr).

Once lithogenic, grain size, organic matter and diagenetic processes have been considered as explanations for behaviour, there are still a number of parameters (Pb, Zn, Cd, Hg, PCBs and PAHs) whose presence can be explained by anthropogenic influence and a couple (Ca and Zr) that might have a human impact influence on the their presence. The pollution input of heavy metals has been decreasing in recent years, as shown by a decrease in metal concentrations towards the surface of the core. However, PCBs and PAHs do not seem to exhibit the same obvious trend. This could be due to their persistence in the environment and the wide variety of sources for these compounds.

This supports the theory that Mersey is a polluted ecosystem and even though things appear to have been improving in recent years there is still a store of these pollutants within the system which have the potential to be remobilized (Fox *et al.*, 1999; Harland *et al.*, 2000; Martino *et al.*, 2002; Ridgeway *et al.*, 2003).

CHAPTER 9
CHANNEL CORE DISCUSSION

The processes acting on this core in terms of provenance and sedimentation are similar to those acting on the Upper Marsh core, although the effect of vegetation is less developed and tidal action is likely to be stronger. The overall trends observed in terms of inter-parametric relationships appear to be weaker, probably due to the location of the core in a much more dynamically active part of the estuary. As in the Upper Marsh core, in order to identify the anthropogenic influence on the sediment it was first necessary to eliminate factors controlled by natural influence such as mineral content, grain size and organic matter effects.

9.1 The Influence of Sediment Composition in the Channel Core

The relatively stable concentrations of Al downcore indicate that it is present at natural background concentrations, as does the fact that it is below ASV. It shows weak positive correlations with Si, Ca, SIRM/ARM and % very coarse silt indicating that there is a lithogenic control on its concentration (Velde *et al.*, 2003).

Ca is above ASV and decreases slightly downcore. It has a weak positive correlation with Si and Al which suggest a lithogenic control on its concentration (related to the local geology of the region) and coarse grained control and a weak negative one with Pb which is possibly due to Pb being associated with finer grained sediments. Ca shows weak negative correlations with Zn, Hg, χARM and ARM which all support the theory of a grain size control on its presence. The weak positive correlation it has with Sr could be due to the presences of shell material in the sediment (Ridgeway *et al.*, 2003).

Zr concentrations are much higher in the top part of the core than they are lower down (from about 8cm depth). It is above ASV and correlates positively (and this is supported by the PCA scatter plot) with lithogenic matter (Al, Si) (Boyle, 2001) and negatively with Fe, S, Zn, Br, Rb and Pb. It also shows a weak positive correlation with LOI which suggests that its negative relationship with the metals is not related

to organic matter content and could be related to grain size (if the organic matter is particulate organic matter associated with the larger grain size fractions).

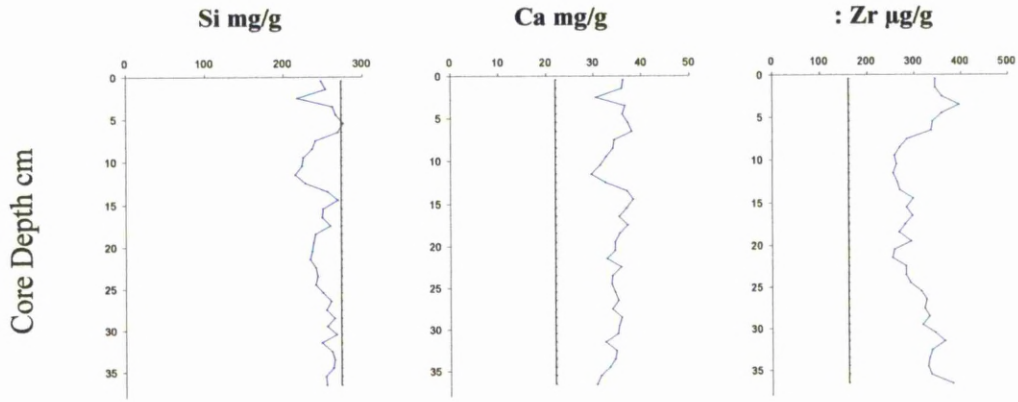


Figure 47: Si, Ca, Zr Profiles.

Both Pb and Zn show weak negative correlations with Ca and Zr which could be interpreted as showing that their presence is not due to lithogenic input to the sediment, as Ca tends to indicate coarser grained sediment or biogenic/lithogenic material. Yang and Rose (2005) reported that a negative correlation between Pb and Ca was often due to dilution of the trace element by $CaCO_3$ in the sediment.

9.2 Organic Matter Behaviour in the Channel Core

The organic matter content of the sediment is low. There is an overall decrease in the organic matter content of the core with increasing depth. However there are a number of fluctuations in this trend. The organic matter concentration decreases sharply in the first 5cm of the core. This could be due to dilution of the organic matter by disturbance of the surface sediment during tidal inundations. It then shows an increase to around 10cm, at which point it begins to decrease again and does so to 18cm where there in another increase (to 23cm) followed by a decrease towards the bottom of the core, which is probably related to decomposition of the organic matter taking place over time (Williams *et al.,* 1994).

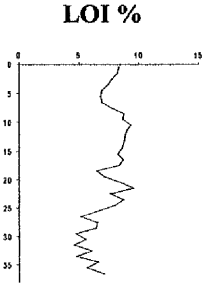


Figure 48: LOI.

9.2.1 The Influence of Organic Matter on Element Trends

Mn has a positive correlation with the finer grain size fraction and with LOI, suggesting that it is related to the organic matter content rather than a lithogenic control. This is supported by weak negative correlations with the coarse grain sized fraction and Si. Its positive correlation with Br and Cl could be due to the organic matter relationship or due to a marine source for those metals. Organic coatings on sediment have a tendency to be rich in ferromanganese oxyhydroxides (Luoma and Davies, 1983; O'Reilly Weise *et al.,* 1995). Br concentrations show a downcore decrease and are well above ASV. It strongly correlates with Mn and LOI indicating a strong organic matter control on its presence (Harvey, 1980). The weaker correlations with fines and Fe support this, as do the negative correlations with parameters that would support a lithogenic and coarser grain size control theory (% sand, Si, Zr, Al). Fe shows a weak positive correlation with LOI which suggests an organic matter control on its presence.

The decrease in Ca at the top of the core corresponds to a decrease in organic matter content, which could cause decalcification to occur as the pH lowers (Luther and Church, 1988).

Cl values fluctuate considerably with depth and it is weakly positively correlated with S, LOI, Pb, Mn, Rb, χARM, χARM/SIRM and χARM/χlf (strongly with Fe) and strongly negatively correlated with Zr (weakly with Si and SIRM/ARM). The Cl concentrations are probably related to finer grained sediment concentrations and to the presence of organic matter in the sediment, which decreases with increasing depth. The fact that it is well above ASV could be due to the influence of Cl in seawater from the estuary.

Sr values are below ASV and fairly constant downcore. It shows a weak positive correlation (supported by the PCA data) with Mn, Br and LOI and other indicators of an organic matter control and it is weakly positively correlated with fines suggesting a fine grain size control is also operating.

9.3 Grain Size Effects in the Channel Core

The slight downcore increase in grain size is a result of the increase in the proportion of the sediment made up from the sand fraction and a decrease in the finer grained mud fraction. The mud fraction is the largest contributor to the overall grain size and this is similar to what was found by Ridgway *et al.* (2003) and to what is seen in the Upper Marsh core. However, unlike the Upper Marsh core the % of sand is increasing downcore, which could be due to the base of the core being deposited in more dynamic conditions.

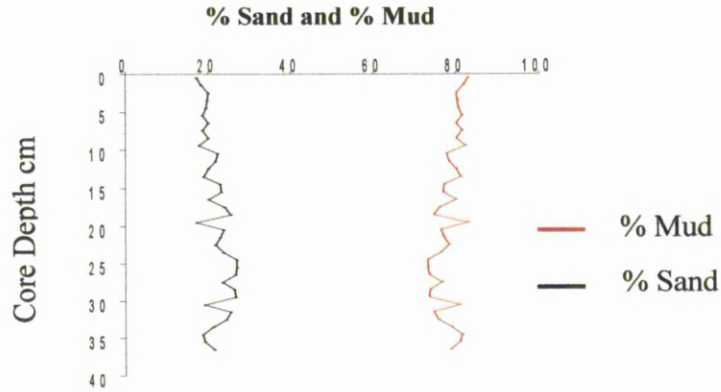


Figure 49: Grain Size.

Si shows weak positive correlations with Al, Ca, Zr, SIRM/ARM and % very coarse silt. All of these tend to be present with coarser grained sediment or are at least indicative of a mineral contents association (Boyle, 2001). It also shows weak negative correlation with Fe, Mn Cl, Br, Rb and a weaker one with LOI, which tend to be found with finer grained sediment. This is supported by a weak negative association with the finer grain size fractions. The negative correlation Si has with χARM, χARM/χLF and χARM/SIRM also indicates its concentration increases with

increasing grain size. Sr has a weak positive correlation with Ca suggesting a possible calcareous rock or shell input to the sediment (Davidson *et al.*, 2005).

Ti values are fairly consistent (and just below ASV) which suggest that there is very little variation in the mineralogy and grain size of the sediment. It shows a strong positive correlation with K and both tend to be indicators of fine grained sediment such as clays and silts.

Fe has a negative correlation with Zr (and a weaker 0.05 level one with Si) which is usually present alongside coarser grained material. A positive correlation with fine grain size parameters such as χARM, χARM/SIRM and χARM/χlf supports the suggestion of a grain size control on its presence. This could be due to the Fe forming surface coatings on the smaller grain side particles ((Luoma and Davies, 1983).

S has a strong positive correlation with % fine sand and weaker positive one with mean grain size, % sand and weak negative correlations with finer grain size fraction indicators such as % mud, which indicate any grain size relationship is with the coarser fractions.

Pb, Zn and Cd all show weak positive correlations with % sand suggesting that at least some of the reason for their correlations with each other is due to a grain size influence. The association with the coarser grain size fractions have been shown by other authors (Hughes 1999; Cundy *et al.*, 2003) to be a result of mining inputs of slag and smelting in the region (Fox *et al.*, 1999; Harland *et al.*, 2000).

Rb concentrations decrease in first 5cm downcore then show considerably fluctuation over the rest of the core and are below ASV. It shows positive correlation with the organic rich fines and weak negative correlations with Si, Zr and SIRM/ARM (indicators of coarse grain mineral matter) and Rb had been shown to bind to fine grained clay minerals (BGS, 1997).

9.4 Channel Core Magnetic Results Discussion

The decrease in the magnetic parameters χARM, χARM/SIRM and χARM/χlf downcore indicate a slight increase in grain size and the peak in grain size at 9-12cm could possible indicate an increase in water flow bringing in coarser grained material when that part of the core was deposited. The weak positive correlation χlf has with the coarser grain size fractions and SIRM, SIRM/ARM and Soft, and weak negative ones with the finer grain size fractions, ARM, χARM/SIRM and χARM/χlf indicate that the magnetic fraction is preferentially found in the larger grain size fractions

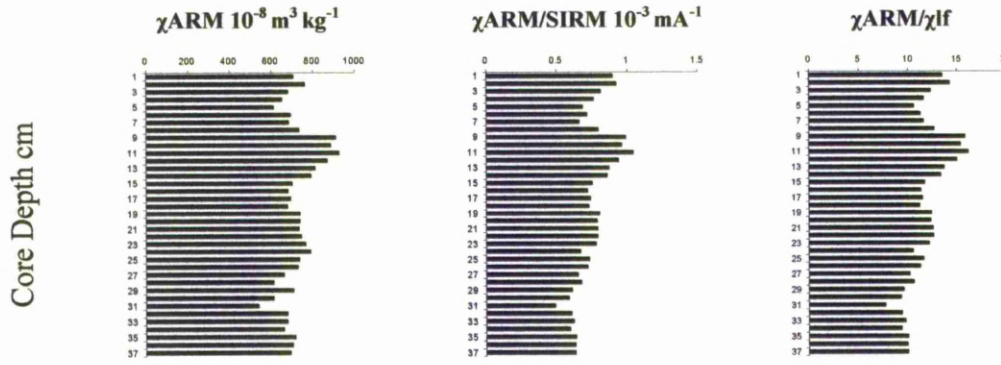


Figure 50: Magnetics Profiles.

It would appear from the values of SIRM/χlf that the dominant mineral is magnetite (Thompson 1980). HIRM and Hard% values are fairly constant with depth but both show a large peak at 7cm suggesting a peak in the haematite/goethite concentration.

Soft values increase downcore with peaks at 7cm and 24cm indicating an increase in ferromagnetic minerals. As in the Upper Marsh core %FD values are low, which would suggest that the bulk of the magnetic signal is from non-soil sources (Thompson and Oldfield, 1985; Scoullos and Oldfield, 1986).

9.5 The behaviour of Elements and Persistent Organic Pollutants in the Channel Core

Mn concentrations are around that of ASV suggesting that it has not been enriched due to a pollution input. The decrease in Mn values at 25cm appears to be associated with a decrease in Fe values (the 2 metals positively correlate). It is possible that this is the redox zone (Cundy and Croudace, 1995) and it is lower than in the Upper Marsh core due to the more dynamic nature of the location of the Channel core allowing oxygen to penetrate deeper into the sediment. The higher concentrations found towards the top of the core could indicate the formation of Mn oxyhydroxides (O'Reilly Weise *et al.,* 1995).

Fe shows a weak positive correlation with Mn, S and Br which suggests a diagenetic control on its presence. Fe has a strong positive correlation with Cl which is either an indicator of a marine control on Fe (this is supported by the weak correlation with Br) or an indicator of a pollution control on Fe. The low concentrations suggest that it has not been affected by pollution, but that its concentrations are related to the natural background levels in the region (BGS, 1997). Sr has a weak positive correlation with Fe which suggests (along with the Mn relationship) a diagenetic control. The lack of correlations with other trace metals is similar to that found by Turner (2000) and probably due to the strong currents in the area widely dispersing the fine sediment and having a buffering effect on the relationships.

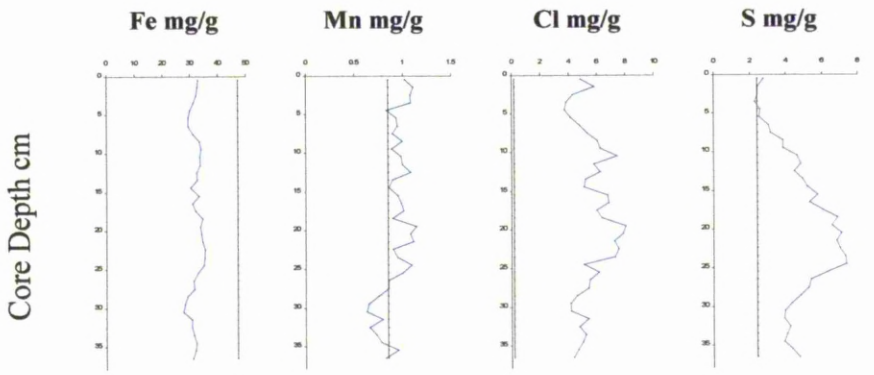


Figure 51: Element Profiles.

The weak negative correlations Al has with Fe and Mn could indicate that it is not being remobilised by any diagenetic activity taking place in the sediment (Shiller and Frilot, 1996). The weak positive relationship Br has with Cl is probably due to a marine influence on their presence.

After a fall in concentration in the first few centimetres, S shows an overall increase in concentration with depth to 26cm when levels start to decrease. This could indicate the location of the sulphate reduction zone (Rae, 1997). As in the Upper Marsh core the association found between S and metals (Fe, Cl, Pb, Zn, Rb and Cd) could indicate the formation of insoluble metal sulphides (McCaffrey and Thomson, 1980; Zwolsmann *et al.*, 1993; Cundy *et al.,* 2003), as well as a grain size control and a possible pollutant input to the system (Alloway, 1995), perhaps from mining activities upstream.

K values are fairly consistent. It is below ASV and shows a strong positive correlation with Ti and weak ones with Fe, Pb, Zn, χARM and ARM which suggest that there is very little variation in the mineralogy and grain size of the sediment. The weak correlation K has with Pb, Zn and Fe could be occurring by chance or could suggest a weak pollution input to the sediment, as K is used in many chemical and medical applications

Pb, Zn and Cd show an increase in concentration with depth and are all above ASV. A similar downcore trend is also shown by Hg, however, its concentrations fluctuate a lot more in top part of the core than those of Pb, Zn and Cd. Pb and Zn have a strong positive correlation with each other (and the PCA scatter plot shows an association between them), a weaker positive correlation with Cd and a very weak one with Hg. This indicates that there is a pollution control on their concentration (supported by the fact that the region has low natural levels of Pb (BGS, 1997). This can also be related to the increase in magnetic minerals which is supported by positive correlations with an increase χlf and SIRM). They also all show weak positive correlations with S which would indicate a possible precipitation of metal sulphides being another contributor to their relationship (McCaffrey and Thomson, 1980; Cundy *et al.,* 2003). Concentrations are similar (if slightly lower) to those seen in the Upper Marsh core and by Langston (1986).

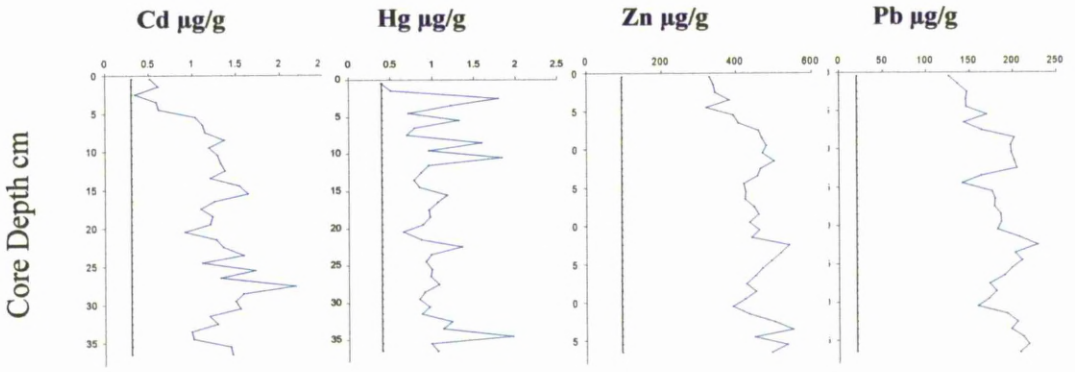


Figure 52: Pollution Metals.

Pb has a weak positive correlation with Fe and K which could be due to it being associated with ferromagnetic coatings on the sediment grains. It is also possible that this relationship with Fe is due to post-depositional processes affecting its concentration. Zn is also weakly positively correlated with K (and very weakly with Fe).

Hg also shows a weak positive correlation with Ni which could indicate a pollution source for Ni. Ni values fluctuate downcore and are below ASV. Ni background levels in the area are low (BGS). The Mersey Estuary has history of high levels of mercury due to the releases from the chlor-alkali industry (Airey and Jones, 1982, Rae and Aston, 1982). Hg levels fluctuate widely in the top part of the core but are more stable below 13cm depth, except for two peaks at 23cm and 35cm and a dip at 21cm.

The gradual decrease of Zn, Pb, Cd and Hg with decreasing depth is similar to what was found by Fox *et al.* (1999) and may relate to past pollution discharges into the Mersey which have been lowered in recent years due to stricter discharge regulations.

9.8 Chapter Summary

The correlations shown between parameters in the Channel Core are weaker and the levels of most parameters in this core fluctuate a lot less than those in the Upper Marsh Core, probably due to the higher levels of mixing that occur in this area. The lower levels of fluctuation between parameters could account for the lower correlations or they could be an indication of a high level of disturbance due to a combination of bioturbation and physical mixing homogenising the conditions. This is possible as this core is nearer to the estuary and will be subjected to more physical disturbance by tides and increased or decreased water flow. This could mean that any relationships between parameters are disrupted and possibly removed from the sedimentary record or that the pollutant input into this core have stabilised (Valette-Silver, 1993; Cundy *et al.*, 2003).

The dominant magnetic mineral appears to magnetite, with a contribution from haematite and goethite. As in the upper marsh core a number of metals can be seen to have a lithogenic control on their behaviour (Al, Si, Ca, Zr) and grain size (which increases down core) affects the concentration of others (Ca, Zr, Si, Ti, K, Fe, S, Rb, Pb, Zn Cd). The influence of organic matter is another factor that affects the behaviour of metals in this core (Mn, Br, Cl, Fe, Rb) and diagenetic processes seem to be working on Fe, Mn and S. Even though there is a change in grain size and organic matter content downcore, they are not large enough to account for the metal profiles found and the most likely reason for the increase in pollution metals (Hg, Zn, Cd, Pb, and to a certain extent Ni) downcore seems to be anthropogenic activity in the region.

CHAPTER 10
SPEKE HALL LAKE DISCUSSION

As in the two previous chapters a number of parameters were measured for this core and they are discussed here. This chapter considers the factors controlled by lithogenic content, organic matter and grain size effects and then looks at the potential influence of anthropogenic pollution inputs to the core. It also compares the core taken for this study with data collected for another study at the same location and the differences between the extracted and unextracted metal data.

10.1 Speke Hall Lake Comparison of Treated and Untreated Element Results

There was a significant difference between the values of all the pre-extracted (treated) sediment and the untreated sediment except for Ba, Cd, Pb, Y and LOI. It was decided that because of this, all the statistical analysis using the metal data would be carried out with the untreated sediment results. This was because most other studies using metal XRF and FAAS data have not used sediment which has been pre-extracted for PCBs or PAHs, therefore, in order to be able to make a comparison with other results we needed to use the untreated metal. It was thought that the difference in values could be due to the solvents used in the extraction process coating the sediment and causing the XRF to give different results. It had been expected that the sediments that had been pre-extracted would have lower metal levels due to liberation of the metal by the ultrasonics, however this was not the case. In fact, with many of the metals the extracted sediment showed higher levels than the unextracted sediment. It is possible that the variability within each sediment sample could be giving the results, or that the ultrasonic extraction released some of the more tightly bound metals from the sediment enough for them to register higher concentrations on the XRF.

10.2 The Influence of Sediment Composition in Speke Hall Lake

Al concentrations in the Speke Hall core are very low and well below ASV. As in the other cores the weak positive correlation with Si and the strong correlation (and grouping in the PCA scatter plot) with Mg (which is another lithogenically controlled element), Ti, K χARM, SIRM/χlf and ARM suggest its presence is related to natural inputs rather than a pollution input (De Vos *et al.,* 2006). The strong negative relationship with LOI would suggest that the Si is not related to organic input and more to the mineral content of the sediment (BGS, 1997; De Vos *et al.*, 2006).

Si shows a gradual downcore increase in concentration and is well below ASV. It shows a weak positive correlation with Al, Ti, Mg and Zr and weak negative correlations with LOI. These correlations indicate a lithogenic control on its presence related to the geology of the area. The grain size correlations and magnetic data indicate that Si levels are related to the finer grained particles and this is supported by increase in Si downcore being accompanied by a decrease in mean grain size.

Ti is well below ASV and has a stable downcore profile. It shows a strong positive correlation with K and weaker one with Zr, χlf, χARM, HIRM, SIRM and a strong negative one with S and weaker negative ones with Mn and P. These correlations suggest that there is a grain size (larger fraction) and lithogenic factor controlling its concentration in the sediment.

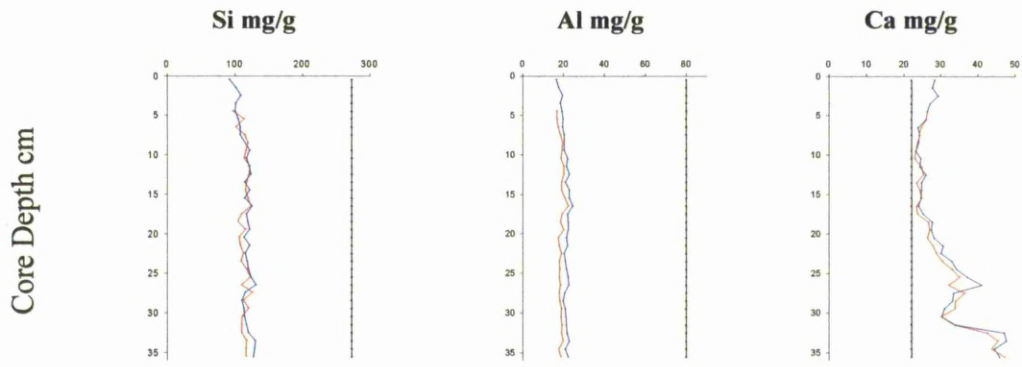


Figure 53: Si, Al, Ca Profiles.

The strong correlation Ca has with Sr could be an indicator of calcareous rock input into the sediment (De Vos *et al.*, 2006), or it could be due to the source being the shells of aquatic organisms (Ridgeway *et al.,* 2003). The peaks towards the bottom of the core could be related to the formation of secondary carbonate minerals due to an increase in alkalinity caused by sulphide reduction (Zwolsman, 1993). The decrease in concentration at the top of the core could be due to decalcification taking place due to a lowering of the sediment pH caused by decomposition of organic matter (Luther and Church, 1988).

10.3 Organic Matter Behaviour in Speke Hall Lake

As expected, LOI has a weak positive correlation with TOC (both are measures of the organic matter present in the sediment). Both are high and show a decrease towards the bottom of the core, probably due to bacterial breakdown of the organic matter (Meyers and Ishiiwatari, 1993). TOC has been shown by Tyson (2001) to be affected by autochthonous organic matter, inorganic dilution, allochthanous organic matter and decomposition of the organic matter during early diagenesis. Lower values of TOC in the top few samples could be due to a change in the amount of organic matter entering the lake, e.g. clearing of vegetation surrounding the area, or a reduction in primary productivity within the lake due to a reduction in nutrients entering the lake, or even a change in the amount being washed into the lake in recent years due to a change in the drainage pattern of the area (although there is no evidence of this). The high levels are probably related to the location of the lake in woodland with a lot of vegetation producing leaf litter which often ends up in the lake, or possibly to changes in the level of the lake which would control the area covered by the marginal wetlands. Organic matter also shows weak positive correlations with % medium sand indicating that the organic matter is associated with that grain size fraction and it could, therefore, be present as particulate organic matter.

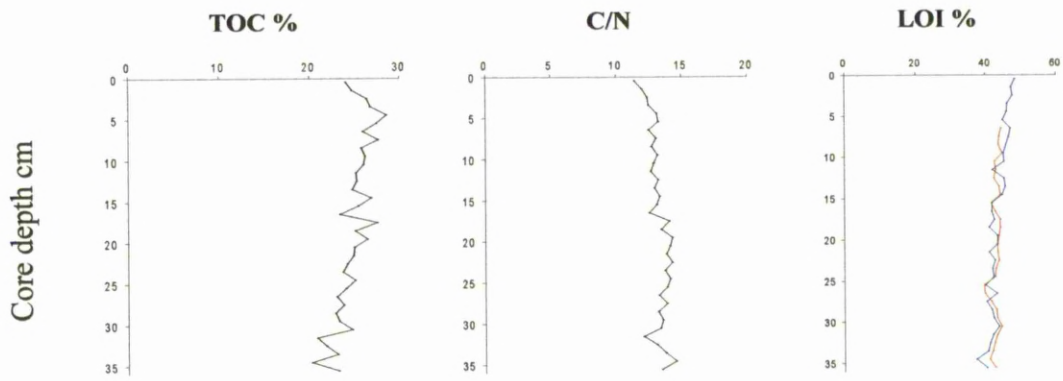


Figure 54: Organic Matter Profiles.

Speke is a relatively shallow lake, which means that the length of time it takes for organic matter to reach the bottom and be incorporated into the sediment is relatively short. This is also a contributing factor to the high levels found in the sediment (~40% LOI and ~30% TOC) (Meyers and Ishiiwatari, 1993). The C/N ratio of between indicates a mixed source of organic matter including both non-vascular aquatic plants (e.g. algae) and vascular land plants (e.g. trees from the surrounding area) (Meyers and Ishiiwatari, 1993), which would be expected given the nature of the lake's location. This is supported by the relatively coarse grain size of the lake sediments, which would suggest a lot of locally derived surface wash of organic matter and coarse particles. Organic matter can be found either as surface coating on the sediment or as separate particles. If present as surface coatings, it presents a larger surface area and has a greater ability to accumulate trace elements (Mirlean *et al.*, 2003). The increase in the C/N ratio towards the base of the core suggests diagenetic remodification of the organic matter (Pratono and Wolff, 1998; Meyers and Ishiiwatari, 1993) or possibly a change in the source of the organic matter. A lack of strong correlation with metals and organic pollutants (PCBs and PAHs) and organic matter could indicate a variation in the source of the organic matter with time, i.e. a change in the dominant vegetation in the surrounding area, or enhanced algal primary productivity within the lake (Luoma and Davies, 1983).

10.3.1 The Influence of Organic Matter on Downcore Trends in Element and POP Concentration

Organic matter has weak negative correlations with Fe, Mn, S, P, Br, Cd, Cu, Pb, Y, Zn, finer grained particles and magnetic indicators of particle size. This would

suggest that the concentrations of these metals are linked to either a lithogenic or pollution input to the sediment rather than an association with organic matter. However, as the majority of the sediment is coarser grained material then that could explain why here is a negative association between LOI and the finer grained particle sizes – the relationship is being masked by the larger proportion of coarser material.

The weak positive correlation K has with TOC suggests a possible organic matter control on its presence. Rb concentrations are below ASV and are fairly constant downcore. Rb correlates positively with organic matter (TOC, LOI) several metals and several PCBs. The negative correlation with the metals and PCBs could be due to the apparent association Rb has with the coarser grain size fraction which could be due to the organic matter being present as larger particulate organic matter.

10.4 Grain Size Effects in Speke Hall Lake

The sediment was a mix of fine and very fine sand and the unimodal distribution indicated that it was dominated by one particle size fraction and this is supported by the grain size frequency leptokurtosis. The negative skewness also supports the mix being that of finer grained sandy material and supports the idea that there is significant inwashing of material from the surrounding area. The decrease in grain size downcore could account partially for the increase in metals and organics downcore, due to their preferential adsorption to smaller particles. The majority of the sediment is sand with some mud and no gravel. There is an increase in the proportion of mud towards the bottom of the core.

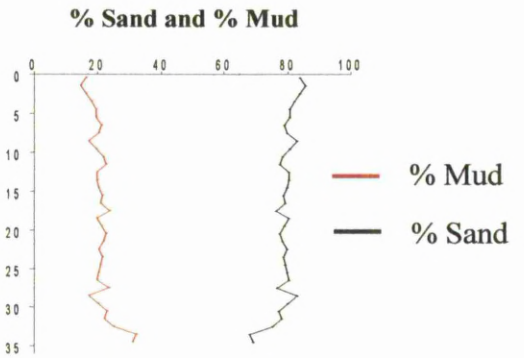


Figure 55: Grain Size Profile.

Ca has positive correlations with fine grained sediment parameters, indicating that its concentration is related to finer grained sediment input. This is supported by negative correlations with coarse grain size fractions.

The below ASV concentrations of K indicates that it is present at natural background levels for the area and has not been enriched via pollution input. K shows strong positive correlations with Ti and Rb, and weaker ones with the coarse grain size fraction as well as with magnetic grain size indicators. K, Ti and Rb are normally associated with the finer grain size fraction, but in this core it seems they are associated with the coarser grained material. This could be due to the relatively coarse grain sizes present in this core. The weak negative correlations with pollutant metals supports the argument that the presence of K is not due to a pollution relationship but is probably due to grain size effects related to larger grain sizes and also to natural lithogenic inputs.

Mg concentrations are below ASV and fairly stable downcore. It shows weak positive correlations with coarser grain size parameters (% sand) and metals that tend to have a coarse grained associations. It shows weak negative correlations with some of the organic pollutants (PCBs and PAHs) which could be due to the grain size influence.

It would appear that there are strong grain size controls on the Mn concentration (supported by PCA scatter data) with positive correlations with the finer grain sized fractions and negative correlations with the coarser grain size fractions and metals such as Ti and Zr, which tend to be associated with the coarse fractions. This is likely due to Mn forming surface coating on the finer grained size fractions (Luoma and Davies, 1983). The positive correlations it shows with metals could indicate that they are being remobilised by diagenetic process and precipitating out as metal oxides. It also shows a strong negative correlation with TOC. Mn has a weak negative relationship with a number of PCBs which could be due to a grain size influence on their presence within the sediment. The low values are due to the natural background levels in the regions (BGS, 1997).

Fe shows positive correlations with the finer grain size fraction and weak negative correlations with coarse grain size indicators such as % sand and Zr. Fe is known to form surface coatings on the smaller grained sediment (Luoma and Davies, 1983).

Sr values are below ASV and stable downcore. It shows positive correlations with fines, SIRM/ARM and SOFT/ARM, suggesting a fine grain size control on its presence, as was found by Liszewski *et al.* (2000). This could at least partially explain the correlations it shows with Mn, As, Ba, Cd, Cu, Ni, Pb, Zn and V. Ba shows a large number of positive correlations and negative correlations and it would appear from these relationships that there is a fine grain sized fraction control on its presence.

Rb correlates positively with the coarser grain size fractions (% sand) and negatively with finer grain size fractions.

Many of the PCBs have correlations with magnetic indicators of grain size (if not actually with the grain size fraction themselves). The majority of these correlations appear to show that the PCBs are more associated with slightly coarser grains rather than finer grain size fraction as was expected. However, this could be explained if the larger grain sizes are considered to include particulate organic matter to which both the metals and PCBs have formed coatings.

A number of PAHs show a positive correlation with the coarser grain size fraction (% coarse sand and % very coarse sand) and a negative correlation with fines which would suggest that here is a grain size influence on their concentrations. Several PAHs have a weak positive correlation with Zr which could be related to the grain size fraction correlations (Fralick and Kronberg, 1997).

10.5 Speke Hall Lake Magnetic Results Discussion

The positive correlation of χlf and Kappa with Soft and a negative correlation with Hard% indicate that the dominant mineral is magnetite (Thompson, 1980). This is supported by the high values of -300mT (Oldfield and Yu, 1994). Hard % increases

upcore, which suggests that the amount of haematite and goethite increases upcore relative to the magnetite which increases downcore (Dearing *et al.,* 1997; Yang, 1997).

The peaks in χlf, Kappa, SIRM and χARM in the middle of the core indicate that these are areas of the highest concentrations of magnetic minerals. The values of FD % indicate that there is a mixture of SP, SSD and MD grains (Muxworthy, 2001). There appears to be a peak in TOC and % mud at a similar level, which could be an indication of an increase in fine grained organic particles due to reductive diagenesis (see below).

The increase in magnetic grain size ratios downcore supports the grain size data which shows an increase in the percentage of mud downcore and a decrease in the percentage of sand. The correlations between metals and the magnetic parameters appear to be grain size related rather than an indicator of pollution input. In fact, many of the correlations between metals such as Cu, Sr, Ni, Cd, Zn and magnetic indicators of grain size (χARM, χARM/SIRM, χARM/χlf) are negative, which suggests that the metals are linked to large grain size particles rather than the fines. This is the opposite of what other authors have found (Scoullos and Oldfield, 1986; Zhang *et al.*, 2001). This could be due to the dominance of the grain size fraction by sand or it could be due to post-depositional alteration of the magnetic minerals. There is no positive correlation between χlf and the 'pollutant' metals, but there is one with Ti and Zr and these metals along with K correlate positively with SIRM and HIRM. A negative correlation between χARM/SIRM and Ca indicates that these decrease with increasing grain size.

In a core with a high percentage of organic matter, Wheeler *et al.,* (1999) showed a relationship between organic matter breakdown and χ, SIRM and χARM concentration indicating reductive diagenesis due to organic matter breakdown was removing the fine grained biogenic magnetite. Work by Tarduno (1995) showed that in anoxic sediment with a high percentage of organic matter reductive dissolution occurs, affecting the concentration and particle size of the magnetic component. The sediment is initially coarsened by the removal of smaller particles due to their larger surface area to volume ratio. However, in the final stages of this process the

magnetic grain size can become very small due to the remnants of the magnetic grains that are left. This process could have led to the production of small magnetic minerals in this core, which would explain the relationship with the magnetic parameters (and the large peak in magnetic concentration – χARM and SIRM – in the middle of the core), Although neither LOI nor TOC correlate with these parameters to support this, there does appear to be a peak in TOC at a similar level in the core. In this core it is not possible to use magnetic susceptibility as a measure of heavy metal pollution due to the lack of correlations with the 'pollutant' metals.

%FD values are low (almost zero in places) which would indicate that the bulk of the magnetic signal is from non soil sources (Thompson and Oldfield, 1985, Scoullos and Oldfield, 1986). This is due to the fact that the FD% is derived from weathered soils and represents fine grained magnetic crystals that are only present in very small amounts in non-soil derived materials. The positive correlation between Ti, χlf and Soft could indicate that the magnetite is titanium substituted magnetite (Maher and Oldfield, 1999). It is possible that the high organic matter content of the sediment and the variety of pollutant sources to this core – road, traffic, industrial incineration, chemical plant emissions of metals and PAHs – have masked out any specific source of pollutants and any specific magnetic relationship with these pollutants, e.g. Pb and χlf. A similar situation was found by Kapicka *et al.* (1999) in a study of soil pollution and magnetic susceptibility in the Czech Republic.

10.6 The Behaviour of Elements and Persistent Organic Pollutants in the Speke Hall Lake Core

After a slight decrease in concentration from the top of the core to 10cm depth, Ca values show a downcore increase and are above ASV. The strong positive correlation it shows with metals that have a pollution control (As, Cd, Cu, Ni, V, Zn) on their concentration (and weak positive correlation with S and several PCBs) indicate that it also has a pollution input (possibly from industrial development in the area – building developments can release Ca to the environment from concrete and cement usage, as does the addition of lime to soil in agricultural activity) (BGS, 1997). It is

possible the peak towards the bottom of the core could be related to a surge in construction in the local area.

The relationship S has with Fe and Mn suggests a diagenetic control on its presence caused by bacterial sulphate reductions (Zwolsmann *et al.*, 1993; Cundy and Croudace, 1995; Spencer, 2003) and its relationship with other metals could be due to the precipitation of insoluble metal sulphides or an industrial related source of the S (e.g combustion of fossil fuels) to the sediment. It also shows a weak negative relationship with several PAHs, which could be related to grain size effect and TOC levels.

Fe has a similar downcore trend to Mn and shows a strong positive correlation with S and weaker ones with Mn, P, As, Cd, Br, Cu, Ni, and Zn. The positive correlation with the heavy metals (Pb, Zn, Ni, and Cd) could be due to their association with the finer grain size fraction and indicate a diagenetic control on their behaviour. The correlation with Mn and S suggests a diagenetic control on the presence of Mn (O'Reilly Weise *et al.*, 1995). The weak negative correlation Fe shows with various PAHs could be due to them being associated with coarse grain size fraction. It is unlikely that there is a pollution influence on Fe in this core, due to the low levels present and the stable downcore profile (BGS, 1997).

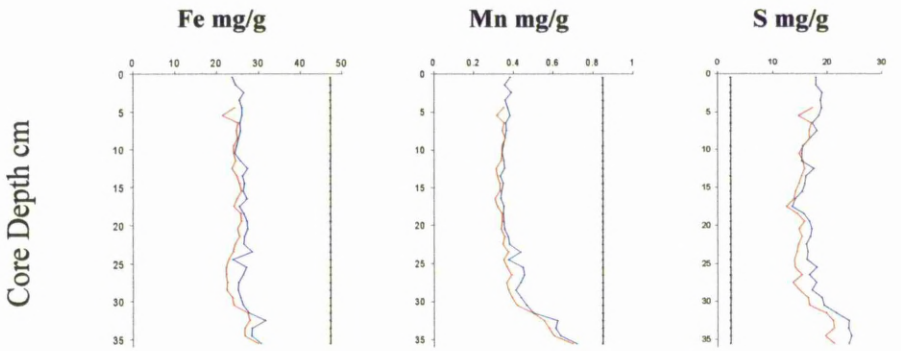


Figure 56: Fe, Mn, S Profiles.

Cr values are below ASV and are stable downcore. Cr shows weak positive correlations with Fe, Mn, As, Cu, Ni, V, Y and PCB 47. These are likely to be related to a diagenetic control on its behaviour. Interestingly, Cr values are lower than ASV despite relatively high natural concentrations in the local area (BGS,

1997). The positive relationship with Fe is likely to be the results of Cr forming complexes with Fe (Turner, 2000).

Br is above ASV and fairly stable downcore. It correlates positively with Fe and negatively with Zr which could suggest a weak diagenetic control on its presence.

Due to low natural levels in the Merseyside region (BGS, 1997), the high levels of Pb found here are likely to be related to the industrial history of the region. The decrease in Pb towards the surface of the core could be explained by the tighter regulation of emissions in recent years including the removal of Pb from petrol. The increase in Pb from the bottom of the core to around 23-24cm could be an indicator of the increased use of motor vehicles in the area in the 1950s and 60s. However, even in the surface sediment Pb is considerably higher than ASV so there is obviously still a pollution input to the area. This could be via surface runoff from contaminated soils in the catchment or atmospheric deposition.

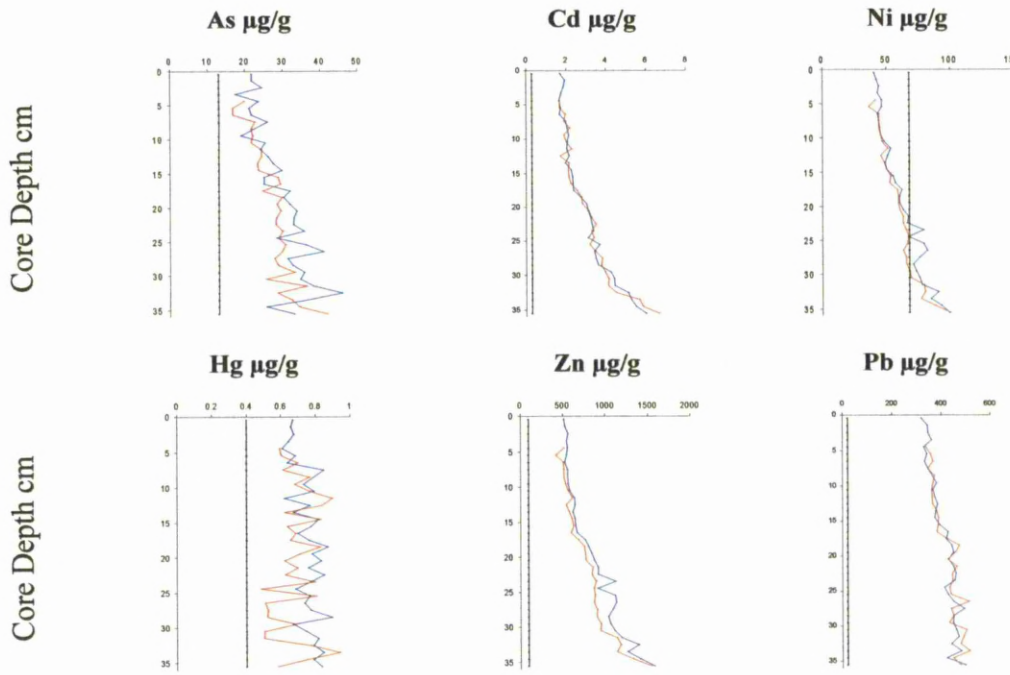


Figure 57: Pollution Metal Profiles.

The other 'pollutant' metals As, Cd, Ni and Zn also decrease towards the surface of the core, which could also be due to a decrease in their release to the environment due to increased regulation, a decrease in industrial actively in the region (e.g.

mining) and more efficient industrial processes. However the only one to drop below ASV is Ni.

Pb, Cd, As and Zn show strong positive correlations with each other as well as with V, Cu and Ni. This would suggest a pollution related link between these metals. However, these metals are often found in the same mineral deposits which could also suggest that the correlations are related to a similar mineral source rather than a pollution influence (Smedley, 2002). They all have positive correlations with % fine sand and % coarse silt, which leads to the conclusion that at least some of their relationships with each other is based on a grain size link. This is supported by the positive correlations they have with SIRM/ARM and Soft/ARM and negative correlations with χARM/SIRM and χARM/χlf. All the above metals show a negative correlation (at different degrees of significance) with organic matter indicators (either TOC, LOI or both). It could be that when an area is heavily vegetated (like at Speke) more of the pollutant metals are stopped from entering the sediment and are trapped on the vegetation. This could also support the theory that the majority of pollution entering the lake comes from airborne sources.

Pb, Cd, As and Zn also all show varying degrees of correlation with various PCBs. This could be due to shared sources or it could be due to a general pollution input to the area. Interestingly, none of them correlate with PAHs, which would suggest either a different source for the PAHs, a different method of deposition or that PAHs behave very differently to PCBs and heavy metals in lake sediment.

Cd, Zn, Pb, As, Ni, V and Cu also all show a positive relationship with Mn whilst Ca, Y and Ba and V, As, Cd, Zn, Cu and Ni have a positive relationship with Fe. Vanadium, Cd, Zn, Cu and Ni also show a positive correlation with S. These positive correlations indicate varying degrees of diagenetic association between the metals. The positive relationships with S could be an indicator of the formation of metal sulphides (McCaffrey and Thomson, 1980) and the ones with Mn, an indication of post depositional remobilisation and are supported by a positive relationship with Fe possibly due to the formation of Mn-Fe Oxyhydroxides (Cundy and Croudace, 1995). Y can be a pollution metal, as it is often released by mining activities and S can be released during Cu smelting, as can As (Rees, 2007). Cd often shows a strong

affinity for clay fractions (BGS, 1997) and its relationship with Pb and Zn is often mining related (BGS, 1997). High Cu levels in the area can be related to mining, smelting and other industrial activities (Harland *et al.*, 2000) and it is absorbed on to the finer grain size fractions.

Of all the metals looked at, Cd is often the most readily remobilised during diagenesis and this could explain its positive correlation with Fe and Mn (Giblin *et al.*, 1980). However, its correlation with the other metals can be explained by common pollution based sources for these.

Ni concentration follows a similar profile to the other contaminant metals and is above ASV towards the base of the core. This supports the conclusion that there is an anthropogenic control on its presence, as natural background levels in the region are low and the decrease toward the surface of the core indicates that discharges to the region have improved in recent years (BGS, 1997).

The fact that As has a positive correlation with the other metals would suggest that the lake has not been acidified as, in acidic conditions, As is known to precipitate out of the sediment but not the other metals (Webster, 1999). Mining is a common source of As contamination – which could explain why it correlates with Pb, Zn and Cu (Bryan and Langston, 1992). Arsenic is strongly sorbed by Fe and Mn oxyhydroxides, which would explain the positive correlation with these elements (Belzile and Tessier, 1990; De Vitre, 1991; Bryan and Langston, 1992; Camacho-Ibar, 1992; BGS, 1997). It is also used in pesticides (sodium arsenite), but this use was banned in the 1970s, which could be one of the reasons for the decrease in concentration towards the surface of the core (Valette-Silver, 1993).

V concentrations are below ASV (regional background level are also low, BGS, 1997) but it shows a similar downcore profile to known 'pollutant' metals (Cd, Zn and Pb) and approaches ASV at the bottom of the core. V can enter the aquatic environment *via* pollution sources, for example, coal and oil combustion, traffic pollution (BGS, 1997) and a pollution control on its presence is supported by a positive correlation with the other 'pollutant' metals and a variety of PCBs. There also appears to be a fine grain size fraction control on it (which could also partially

explain the relationship with the metals) and possibly a diagenetic influence on it (positive correlations with Mn, Fe and S), as V can often form complexes with organic matter and Fe oxyhydroxides. It is often found in magnetite (and the top part of its profile is similar to that of Soft magnetism (BGS, 1997).

Hg shows a slight decrease in concentration towards the surface of the core. Although no correlation was detected between organic matter content and Hg this could be due to the type of organic matter present. In a study of Canadian lakes, Sanei and Goodarzi (2006) found in one core no correlation between Hg and TOC, however, when the relationship between the different fractions of organic matter was investigated a correlation was found between Hg and the more labile free volatile hydrocarbons in the sediment, but not the higher molecular weight hydrocarbons from an algal sources (which are more resistant to diagenetic change). They also showed that in a lake with a large amount of allochthonous organic material there were lower correlations with Hg and TOC. This could be what is occurring in the Speke Hall core. If large amounts of organic matter are entering the sediment from the surrounding area it could be masking out any relationship between Hg (and other metals) and organic matter within the lake. A relationship was found with Hg and TOC from a lake where the organic matter was composed of coal particles and other burning products (Goodarzi, 2006), which would indicate that in this lake the majority of organic matter comes from vegetation, not combustion sources, as there is no correlation with Hg and organic matter and reduced (and in some cases negative) correlations with other metals and the organic pollutants. Concentrations are an order of magnitude higher than have been found in the Canadian study, probably due to the location of the lake being nearer industrial sites.

The correlations between Sr and Mn, As, Ba, Cd, Cu, Ni, Pb, Zn, and V could be due to a pollution relationship (Zn from refining, industrial waste incineration – which could also explain its weak positive correlation with a number of PCBs). It would appear that there is no organic matter control on Sr, as it has a weak negative relationship with LOI and a strong negative one with TOC. Barium concentrations exhibit a slight downcore increase but are well below ASV and it also appears to be related to possible sources of pollution (it can be present due to mining activities and is often associated with Cu deposits and industrial waste deposition) (BGS, 1997).

However the correlations could be purely due to these metals and Ba forming Mn-Fe oxyhydroxides.

The concentration of Zr is below ASV and shows a slight downcore increase to 25cm followed by decreasing concentrations to the bottom of the core. None of the correlations suggest an overall grain size control on its concentration, but the weak negative relationship with Fe, Mn, S, P and Br could be an indicator of a diagenetic and organic matter control on its concentration, There is also the possibility of a weak lithogenic control on it (positive correlations with Si and Ti) and even a positive relationship with several PAHs which could be related to wear and tear on brake pads and therefore indicate an anthropogenic influence on Zr.

Following on from an initial downcore decrease (to 9cm) P shows a constant concentration until 28cm when it starts to increase. It is well above ASV and has a strong positive correlation with S and weaker positive correlations with Fe, Mn and the finer grain size fractions. Fe is usually the main carrier of P in the aquatic environment (Spencer, 2003). P negatively correlates with the larger grain size fractions and Ti, K, Zr and magnetic concentration factors. These relationships would suggest that its presence is controlled by diagenetic processes and the finer grain size fraction rather than by a lithogenic input and large grain size factors (Finney and Huh, 1989). It is also possible that the high concentrations could be linked to a local input factor such as fertilizer use. Positive correlations between P and Fe have also been shown to be linked to the presence of furnace waste (but this usually has a correlation with Ca as well, due to the addition of Ca as part of the process to remove P during the production of iron) (BGS, 1997).

10.7 PCBs in the Speke Hall Lake Core

In general, PCBs appear to show a slight downcore decrease to 10cm depth followed by an overall downcore increase in concentrations. They all seem to have very low sediment concentrations between 10cm and 13cm depth and at 14cm and 24cm depth. It is possible that these low concentrations are related to climatic variation in the region. Either a very dry year with very little water entering the lake, therefore

small amounts of PCBs entered the sediment or possibly a wet year with a lot of material washed into the lake which diluted the PCB signal. However, there are not low values of other parameters at these depths which would be expected if weather changes where the explanation, therefore it is more likely that the low values are due to a change in source of the PCBs, possible a factory or incinerator closing down. The increase from this point to the surface to the core could also be explained by a new source coming on line after this point, e.g. a new incinerator or a change in the major source of pollution from a local to long distance atmospheric transport source It is likely that the decrease in PCB concentration from the bottom of the core to 14cm is due to a decrease in the amount of PCBs being released into the environment as stricter discharge regulations and cleaner technologies came on line.

The overall downcore increase in PCB values supports the theory that the pollution input to the area has decreased in recent years. Concentrations are relatively low but, in recent years, there appears to have been a slight trend to increasing PCB contamination. It is unlikely that this comes from direct industrial emissions due to the banning of the use of PCBs in the 1970s, but it does show the persistency of these compounds. It is possible that this increase could be due to an increase in the decommissioning and disposal (e.g. by incineration) of PCB containing equipment in recent years and, if this is the case, it could be used as an argument against the use of incineration for equipment containing persistent organic pollutants. The increase could also be the result of PCBs leaching from landfill sites or even long range transportation from other parts of the country/world (Holden, 1981). The possibility of long range transport as a source is supported by the fact that the congeners that seem to best show an increase towards the top of the core are the lower chlorinated, more volatile congeners (18, 28, 44, 49 and 52) and these appear to show an increase in their relative percentage contribution to the total PCB concentration in the top of the core (Camacho-Ibar, 1991). This is similar to what was found by Klanova *et al.* (2008) in Antarctic sediment. High concentrations of PCB 28 and 52 can be explained due to the fact that, historically, these are two of the most abundant PCBs produced (Breivik *et al.*, 2002) and the most volatile.

In general, the PCBs show positive correlations with other PCBs indicating a related source. The majority of PCBs show positive correlations with many of the 'pollutant'

metals with Cd, Pb, Zn, Ni showing the greatest number of positive correlations and As, V and Cu also showing correlations with a number of PCBs, whilst Hg has negative correlations with many PCBs. The correlation with metals indicate either a related source from local industry or possibly a related long range source, if the metals are also subjected to long range transport, or it could be due to the metal and the PCBs being associated with the same grain size fraction.

The only PCBs to show a relationship with PAHs are PCB 66, 101, 151, 105 138 PCB 128, PCB 180 and Total PCBs. It is possible these correlations occurred accidentally or that they show a similar source for these compounds or that they are occurring due to both PCBs and PAHs showing the same grain size fraction relationship.

The presence of PCBs at the bottom of the core indicates that the core depth has not reached pre-PCB production depth so, therefore, does not go back further than the 1930s or 1940s, which would support the proposed time line suggested in the metals section above.

10.8 PAHs in the Speke Hall Lake Core

10.8.1 PAH Concentrations

The downcore profile of PAHs is very variable, probably reflecting the variable nature of the sources of these compounds. PAHs enter the environment from natural sources such as burning vegetation, as well as from manmade sources such as vehicle exhaust emissions and incineration (Yunker *et al.*, 2002).

As mentioned in the results chapter there appears to be decreases in concentrations of phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenz[ah]anthracene at 8cm, 13cm, 19cm, 22cm and 32cm. This trend can also be seen in acenaphthene and fluorene, although it is not as obvious. As with the changes in the low concentrations of PCBs, it is possible that this could be due to a short term change in the local climate (e.g. a very wet or very dry year). However,

there is no corresponding change in the metal parameters that would support this theory, leading to the conclusion that a change in the source of the PAHs, rather than a natural phenomenon, is responsible the lower values.

Aside from the correlations with PCBs mentioned above PAHs correlate well with each other. Phenanthrene, anthracene, pyrene, chrysene, benzo[a]anthracene, benzo[a]pyrene and total PAHs have a positive correlation with Fe and S, whilst benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[ghi]perylene have a positive correlation with S and indeno[1,2,3-cd]pyrene has a positive correlation with Fe. These relationships could be an indicator of a potential diagenetic control on PAH behaviour (Benlahcen *et al.*, 1997) or the relationship with S could be an indicator of the source being coal combustion.

High levels of organic matter input have been shown to dilute the relationship between PAHs and TOC and could explain why correlations are low in this core (Pereira *et al.*, 1999). A number of studies have highlighted the importance of atmospheric sources of PAHs and PCBs in small lakes (Gevao *et al.*, 1997, 1998, 2000).

As in the Oglet Bay Upper Marsh core, the higher molecular weight PAHs dominate the distribution and could indicate a combustion source dominating the input (Witt, 1995). There is very little variation in % PAH distribution downcore which could indicate that the sources of the PAHs have not varied in recent years or that there has always been a complicated input of PAHs from a variety of different sources.

The correlations the PAH show with χlf could be due to a combustion source for the PAHs, possible as part of fly ash from coal fired power stations or waste incineration (Morris *et al.*, 1994).

10.8.2 PAH Ratios

The PAH ratios suggest that the major contribution to the area comes from vehicle exhausts with a mixture of gasoline and diesel engines, which is to be expected considering the nature of the location of the lake (Caricchia *et al.*, 1999; Pandey *et*

al., 1999; Oda *et al.*, 2001). However, there is also a combustion source (as indicated by the CPAH/TPAH ratio) and some coal burning contribution (Pandey *et al.*, 1999).

10.9 Comparison of Studies

The presence of PCBs in the deepest part of the Speke Hall core indicates that the sediment is from relatively recent history (post-1930s). No specific dating techniques were carried out on this core, but an attempt was made to date it by comparing a number of parameters with those of other cores taken from Speke Hall Lake (Worsley *et al.*, 2005; Power and Worsley, 2009). Figure 58 shows how the different peaks in the parameters have been linked to try to establish a chronology between the core from this study and those in the other studies that have been arrived at through ^{210}Pb dating. Due to the PCBs indicating that the core in this study has to be from post-1930s, it was decided that this core should be linked in with the sections of the cores from the other studies that corresponded to the same time period. This was done by assessing which of the post-1930s peaks in the Worsley *et al.* (2005) and Power and Worsley (2009) studies could correspond with peaks in the matching sediment parameters this study.

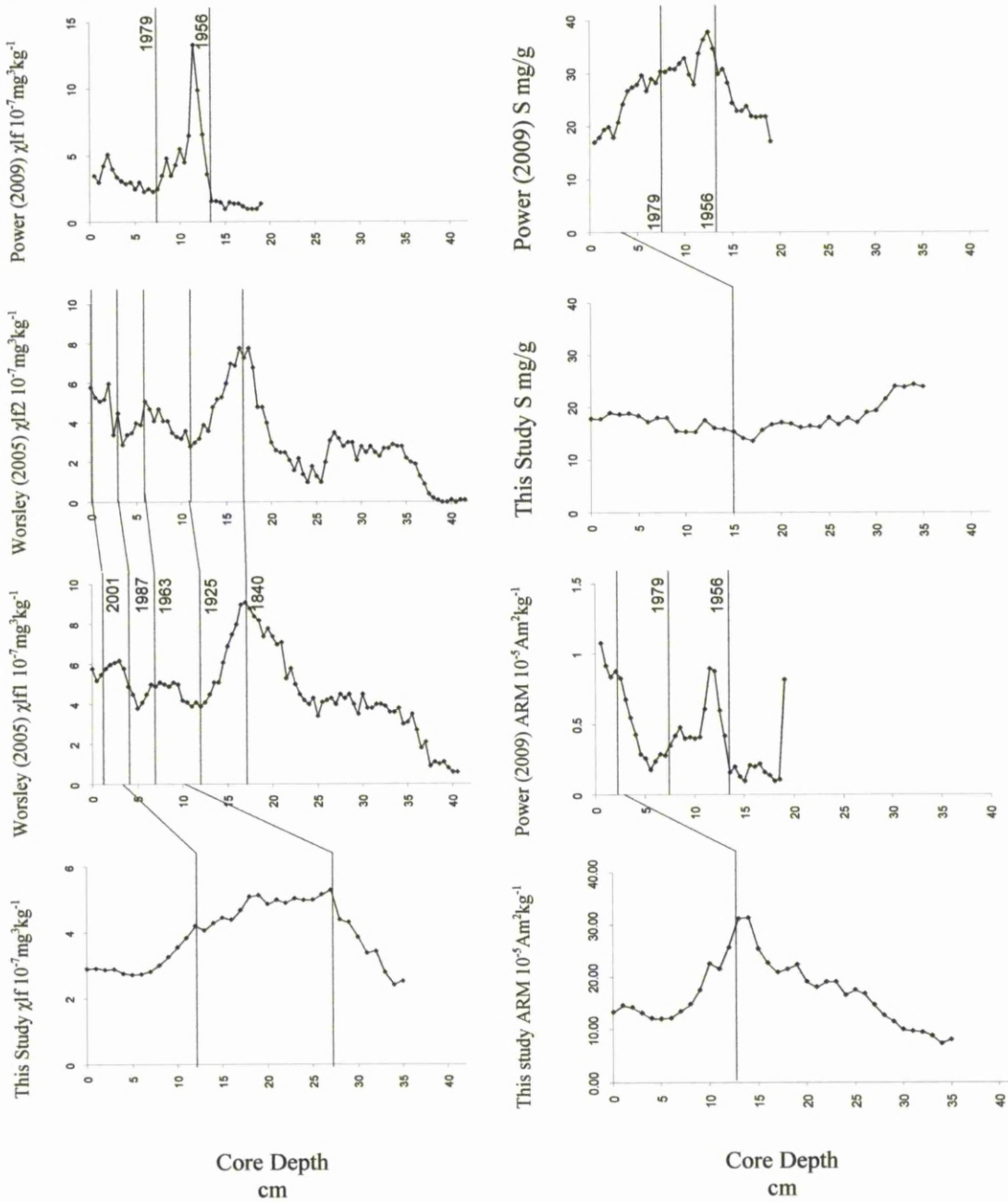
A number of potentially related peaks in the data have been linked by correlation lines (Fig 58). Peaks in χlf from this study at 12cm and 27cm have been linked with peaks in the Worsley *et al.* (2005) study at around 4cm and 10cm depth, and it is likely, based on cross-correlation that the peak in this study at 27cm depth corresponds with that found at 12cm in the Power and Worsley (2009) core. It is possible, based on sedimentation rate from the correlated peaks all ready established, that the peak in the ARM at 15cm in this study corresponds with a peak at around 3-4cm in the Power and Worsley (2009) study. One of the parameters used in the Worsley and Power (2009) study and this study was S, so this was also used to investigate potential cross-correlation between the studies. Due to the smoothness of the S profile from this study, it is difficult to assess whether or not any of the peaks correspond with those found in the Power and Worsley (2009) core. The line on Figure 58 joining the S cores has been plotted based on the depths of corresponding peaks found in the ARM data. Using the same method, peaks in the Pb (at 12cm and

27cm) and Zn (at 14cm) data have been linked with the data from the Worsley *et al.* (2005) and Power and Worsley (2009) cores respectively.

Comparison of the downcore profiles from this study and the other studies (Worsley *et al.*, 2005; Power and Worsley, 2009) show similar trends for the parameters. However, certain peaks in these trends occur at different depths in the studies, suggesting different rates of sedimentation at the different core locations. In this study all the profiles are a lot smoother than those seen in Worsley *et al.* (2005) and Power and Worsley (2009) cores, possibly due to a faster sedimentation rate. From these comparisons (Fig 58) it would appear that sedimentation rate varies within the lake and it is possible that the core from this study is from an area with approximately three or more times the sedimentation rate of the areas the other cores where taken from. If this is the case, then it would suggest that the data in this study are of a higher resolution that that from the Worsley *et al.* (2005) and Power and Worsley (2009) cores. The higher sedimentation rate could be due to the core from this study being from a deeper part of the lake than the cores from the other studies, or possibly located in a section of the lake that receives higher sediment input from the land.

If we accept that the sedimentation rate, in the area the core for this study was taken from, is around three times higher than the other cores then it can be concluded that this core is approximately 70 years old, dating from the mid-1930s. It was decided (based on corresponding peaks in the data – see above) that the upper 15cm of this core corresponded to the top 5cm of the core taken by Worsley *et al.* (2005), whilst the next 15cm of the core matched to the section of their core between 5cm and 12cm. The data from these cores suggests that there is up to a threefold difference in sedimentation rates across Speke Hall Lake. It is not uncommon for different rates of sedimentation to be found larger lakes (Balis and Kalff 1995; Yang 2002) but is strange in a lake of this small size. The core taken by Power and Worsley (2009) appears to have a different sedimentation rate again which seems to vary downcore. The peaks in ARM towards the top of the cores could indicate an increase in the concentration of ultrafine particles present in the environment caused by an increase in air traffic and vehicle usage during the late 20th Century (Power and Worsley, 2009).

The downcore profile of Pb and Zn profiles from our study would appear to indicate that the cores are not deep enough to record pre-pollution input levels (which is supported by the presence of PCBs in the lower parts of the core). There is a large peak in the Power and Worsley (2009) Zn profile which has been dated to 1966. The suggested explanation for this is that the rapid expansion of industrial development occurring in the Halton and Merseyside area at the time, caused a large increase in the pollution load to the area and that the disturbance of the surrounding land by this development released more sediment into the lake. Concentrations of Pb and Zn in the sediment appear similar between the cores.



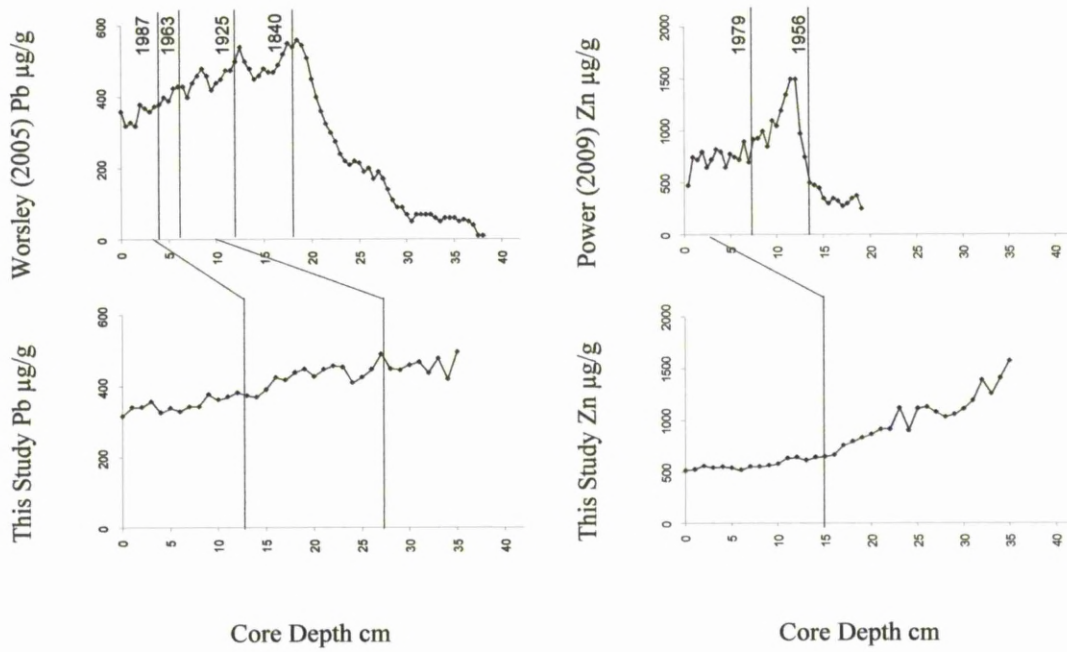


Figure 58: Comparison of Worsley et al. (2005), Power and Worsley (2009) and the core taken at Speke Hall for this study.

10.10 Chapter Summary

A number of studies have used urban ponds and lakes as a method of assessing the pollution history of a region and this core supports the use of these locations. However, it also illustrates that the location of a core within a lake can influence the recording ability of the sediment. Comparison between this core and ones taken by Worsley *et al.* (2005, 2009) shows that the record in this core is much smoother and does not have the same obvious maxima as Worsley's cores. This could be due to differing sedimentation rates between cores or sediment focusing affecting the distribution of the pollution. However, all cores do show that the concentration of pollutant metals (particularly Zn and Pb) are decreasing towards the surface of the core.

In this study there is no correlation between χlf and the pollutant metals making the magnetic record a poor method of measuring past pollution in this case. The peak in indicators of ultrafine magnetic concentration (χARM) in the middle of the core could be showing the final stages of reductive diagenetic breakdown of organic

matter producing ultrafine magnetic particles. It is possible that the high organic matter content of the sediment and the variety of pollutant sources to this core – road, traffic, industrial incineration, chemical plant emissions of metals and PAHs – have masked out any specific source of pollutants and any specific magnetic relationship with these pollutants, e.g. Pb and χlf. The behaviour of the metals seems to be more related to interaction with other parameters (e.g. diagenesis) in this core than it was in the estuarine cores.

Lithogenic processes appear to be responsible for the behaviour of Al, Si Mg, Ti and K, whilst grain size controls are operating on Ca and Mn (grain size decreases downcore). Ca may also have a pollution control operating on it.

Cd, Zn, Pb, As, Ni, V and Cu also all show a positive relationship with Mn, whilst Ca, Y, Ba, V, As, Cd, Zn, Cu and Ni have a positive relationship with Fe. Vanadium, Cd, Zn, Cu and Ni also show a positive correlation with S, which would indicate a diagenetic control on their behaviour. However the correlations Pb, Zn, Cd As, Ni have between each other would support an argument for a pollution effect on their presence. Hg, PCBs and PAHs also have a pollution control. The correlations between the coarse grain sizes and PCBs and PAHs could be due to the presence of particulate organic matter associations

The down-core metal profiles are more stable in this core than in the estuarine cores. This probably reflects the less dynamic nature of the lake environment when compared to the one the estuarine cores are deposited in. Although the concentrations of pollutant metals (As, Cd, Ni, Hg, Zn, and Pb) are decreasing towards the surface of the core, indicating that the pollutant input to the region is also decreasing, they are still present at high levels.

CHAPTER 11
COMPARISON OF THE THREE CORES AND THE PROBLEMS WITH DISEASE INCIDENCE DATA

One of the main strengths of this study is that the same techniques were used to study each core. This allows direct comparison between the results without having to account for differences caused by the use of differing laboratory methods or statistical analysis.

11.1 Comparison of Sediment Cores

Due to their locations, the processes acting on the Upper Marsh Core, Channel Core and Speke Hall Lake core will be different, perhaps less-so for the estuary core sites in terms of provenance (Upper Marsh and Channel). The Upper Marsh core is part of a stable, vegetated saltmarsh, whilst the Channel core is part of the muddy edge of the river and more frequently subjected to tidal disturbance and the Lake core is in a relatively undisturbed area surrounded by woodland. There is no river input to the Lake core and any aqueous input will come *via* overland runoff, whilst the cores from the estuary will receive aqueous input from both the river flow and periodic tidal inundations.

11.1.1 Organic Matter

It can be seen from the data that the amount of organic matter is higher in the core from Speke. This is probably due to the location of the lake, surrounded by trees and marginal wetlands. In all cores there is a downcore decrease in the amount of organic matter present, due to the breakdown of organic matter by bacterial action (Williams *et al.,* 1994). This is accentuated in the saltmarsh where elevation above mean high water leads to the colonisation of the surface sediment by vegetation. Of the three cores, the Upper Marsh data seems to show the most fluctuations in organic matter content. This is likely to be due to the influence of productivity from the saltmarsh, its periodic emergence above the higher tidal levels as it accreted was interspersed with periodic inundations as sea-level rise operated to flood the marsh surface. The more stable profile at Speke is reflective of what is probably a relatively constant

input of organic matter from the surrounding area, There are a few places in the core where organic content drops and this could be due to human activity in the area, e.g. occasional clearing of the vegetation from the edge of the lake or inwash event from the surrounding fields. The ranger at Speke Hall has confirmed that vegetation clearing is done on occasions (as is dragging of the surface of the lake to remove lilies) (Pers comm.).

Concentrations of Ti, Al, K, Zr and Si are higher in the estuary cores than in the lake core. This could be reflective of the lower amount of organic matter in the estuary cores, meaning that there is relatively more lithogenic based material present in those samples. It is also an indication of the finer grain size of the estuary cores as K, Ti, Zr and Al are generally found in clays and silts.

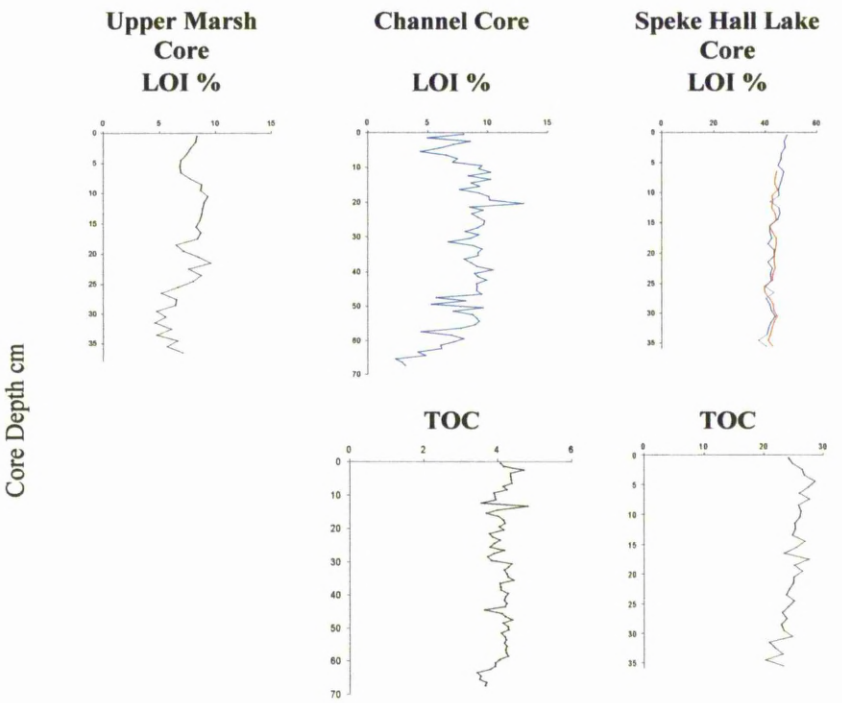


Figure 59: Comparison of organic matter content.

11.1.2 Grain Size

There is a difference in the grain size between the 3 cores. The larger grain sizes are found at Speke, which could be due to the higher concentrations of particulate organic matter in the core or it could be explained by coarser grained sediment being brought into the lake by inwash from the surrounding land. Speke had much higher

levels of organic matter than the estuary cores which could point to the larger grain sizes being particulate organic matter. This is probably due to the difference in the surrounding vegetation distribution. The lake is in a wooded area surrounded by trees which will account for the higher levels of organic matter found in the sediment, whereas the saltmarsh is located in a much more open area with much lower levels of vegetation and, therefore, lower concentrations of organic matter entering the sediment and the decomposition of surface vegetation. The rise and fall of the tide could have encouraged humification of the organic matter of the estuary cores. Another explanation for the coarser grain size found in the Speke core could be high amounts of slope wash bringing in eroded sediment from the surrounding land.

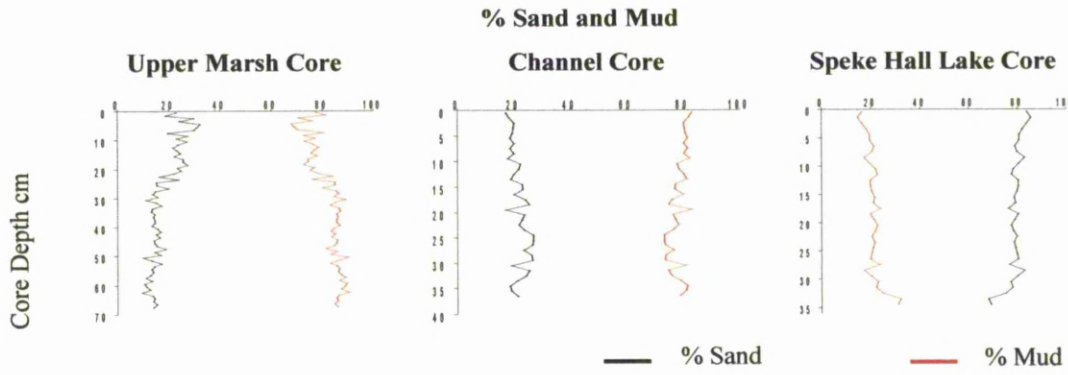


Figure 60: Grain Size Comparison.

The majority of sediment in both the Channel core and the Upper Marsh core is mud, making them both a potentially good source for investigating the historical pollution input to the region (Cundy *et al.*, 1997). However, the more dynamic environment that the Channel core is from means that the record has a much higher potential for reworking at high frequency and, hence, only the general trends remain. It should also be remembered that any pollution record in estuarine sediments could have been subjected to a time delay between releases of the pollutant and its deposition into the sediment so accurate dating might not be possible unless it can be tied in with known pollution events.

11.1.3 Element, PCB and PAH Behaviour

Neither the Channel core nor the Lake core showed evidence of diagenetic remobilisation of Fe and Mn, whereas the Upper Marsh core did, probably because it

was exposed to the air for prolonged periods. The Channel core location was much nearer the river and, therefore, was more likely to be submerged by the tide and affected by increased water flow within the Mersey. This will mean that the sediment will be more subject to erosion than the Upper Marsh core. The Upper Marsh core location was further away from the main channel and, therefore, it is likely that it is only flooded on higher tides.

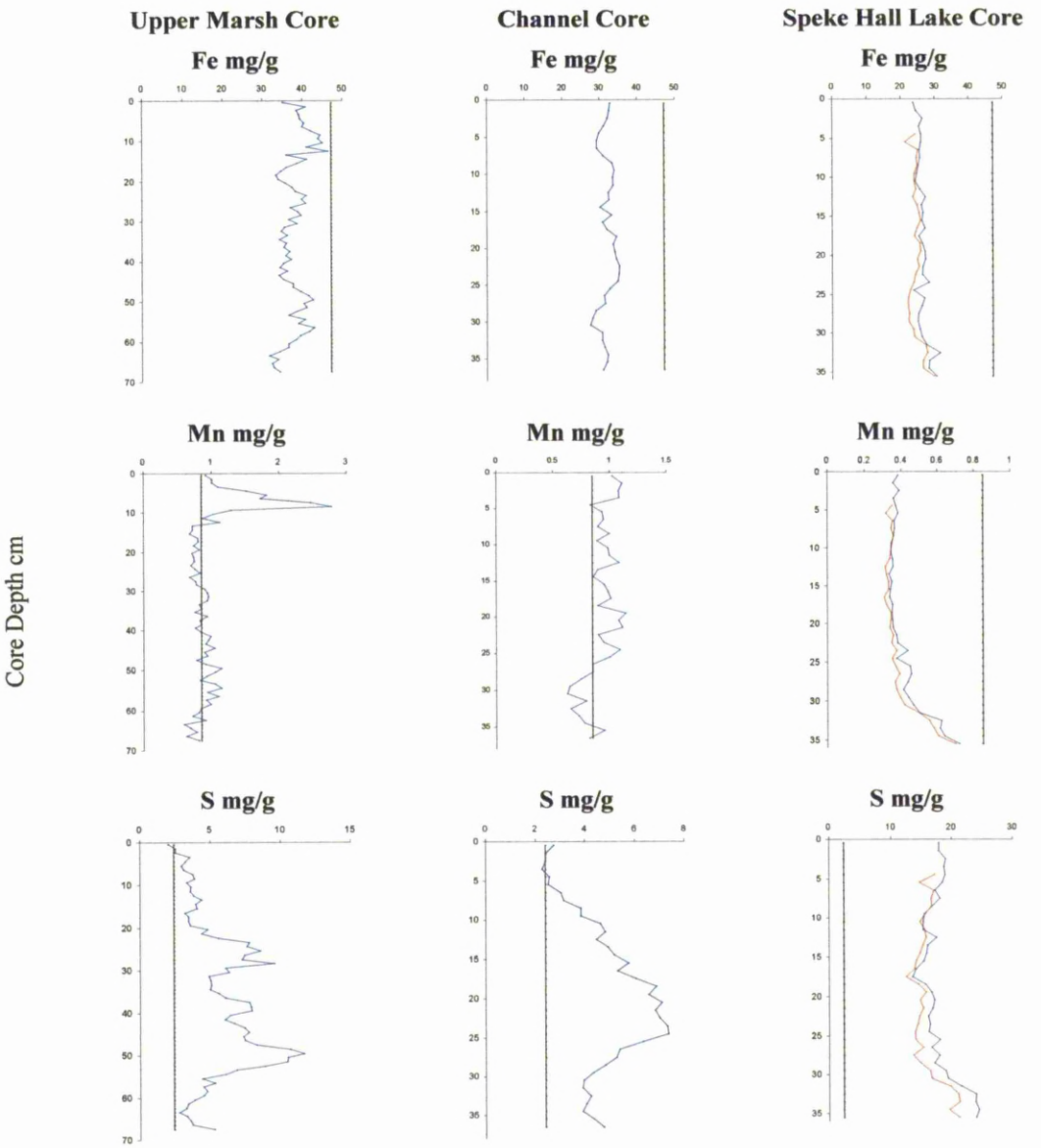


Figure 61: Fe, Mn and S Comparison.

The metal profiles in the Speke Hall core are more stable downcore. This probably reflects the less dynamic nature of the environment they are deposited in. They are

not subjected to the levels of disturbance caused by tidal action and periodic flooding and the atmospheric flux will be more consistent and less likely to lead to a spike in concentrations than the aqueous flux of pollutants. There is no peak near the surface in Mn to indicate post-depositional diagenetic remobilisation.

The increases in S in the estuary cores could indicate bacterial reduction of sulphate. Sulphur often shows a peak just above the sulphate reducing zone (Rae, 1997). There is no really evidence of a peak in the Lake core although there is a mid-core drop in concentration.

It has been suggested by Turner (2000) that lower levels of Pb compared to Zn in the Mersey were due to the differences in transport modes bringing them into an estuary. He concluded that atmospheric sources were the more important source for Pb whereas as aquatic input was important for Zn. If atmospheric sources of these metals are more important than aquatic then that could account for the higher concentrations found in the Speke Hall core. The levels in the estuary cores could be diluted by aquatic inputs and the more dynamic nature of the environment. If the lake has input mainly from organic matter, dusts that settle into the lake and occasionally runoff this will provide a much lower supply of material than the regular inundations the estuary cores will receive from sediment laden tidal waters. This means the potential for 'dilution' by unpolluted mineral matter is much greater in the tidal setting. Interestingly Hg concentrations are highest in the Upper Marsh core, which could indicate that in the Merseyside area aquatic inputs are a more important source of Hg than atmospheric. This would support the theory that large amounts of Hg are stored in the sediments upstream around the river Weaver and Manchester Ship Canal and the remobilisation of these, e.g.by dredging, is leading to a constant supply to the downstream sediment record (Langston, 1986; Harland *et al.*, 2000; Vane *et al.*, 2009). Cd shows the smallest variation between the cores (although concentrations are highest in the Speke core).

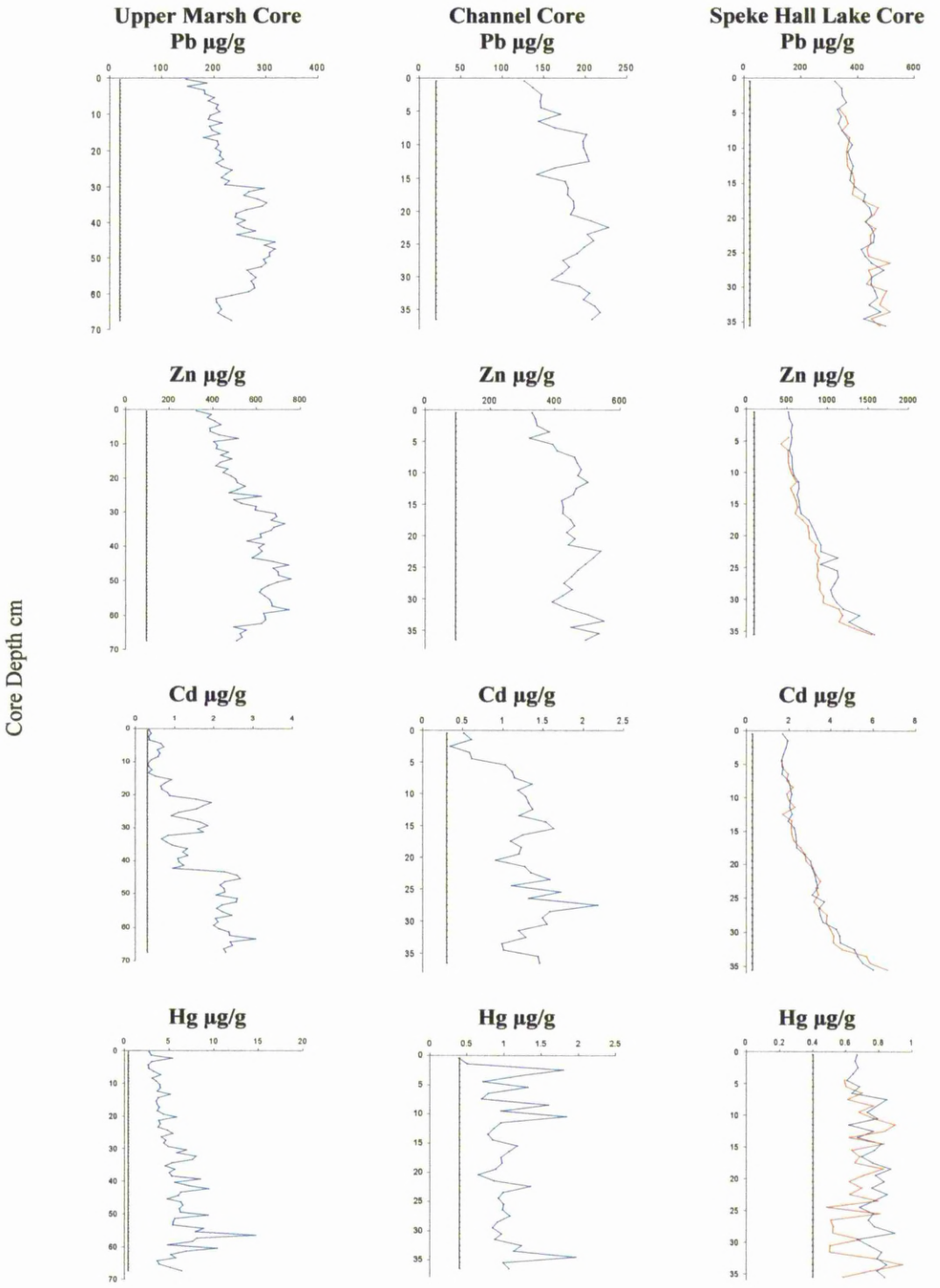


Figure 62: Pollution Metal Core Comparison.

A decline in pollution-related substances in recent sediments as seen in this study, has also been found by many authors (Fox *et al.*, 1999; Cundy *et al.*, 2003; Vane *et al.*, 2007) and these are usually related to either a decline in industry in these locations or improved discharge controls (either cleaner technologies or stricter regulations).

Like metals, PAHs have higher concentration in the Speke Hall core and again this suggests an atmospheric source for these compounds or less dilution by unpolluted, aqueously-derived mineral matter. It is also possible that the higher concentration of organic matter is giving high concentrations of PAHs, due to them forming an association with the organic matter, or even sharing a source e.g. soot particles from incineration (Brownawell and Farrington, 1986). Higher concentrations of PAHs at Speke could be due to the location of the core in a more urban setting close to industry and an airport. Van Metre *et al.* (2003) have shown that rooftops in urban areas can contribute a high level of PAHs to lake sediment in the locality (as well as Zn, Pb, Cd, S, Cu and Ni). Rooftops collect atmospheric deposited contaminants and these can then wash off into the local environment during rain.

PCB concentrations are higher in the estuarine core than in the lake core and their concentrations fluctuate much more than those in lake. This could indicate that the majority of PCB contamination in the region is entering via waterborne routes rather than from atmospheric deposition, or that the levels in the estuary are appearing higher because of the amount stored within the sediment that is being remobilised, recycled and redeposited by the more dynamic nature of the environment.

Support for the source of pollution at Speke being predominantly atmospheric is provided by the increase in the lower chlorinated PCB towards the top of the core as these are the more volatile and most likely to be transported *via* atmospheric processes. Long range atmospheric transport is an important source of PCBs and PAHs to the environment and also to the exposure levels of human (Pereira *et al.*, 2007).

11.2 The Potential for Toxic Effects of the Sediment Pollutants

Levels of pollution in the cores were assessed using Canadian Sediment Quality Guidelines (CSQG) (CCME, 1995) and Soil Guideline Values. Sediment quality guidelines (Tables 5 and 6) have been proposed to allow estimates of the degree of pollution of the sediment to be made and an assessment of the potential for toxicological effects these pollutants have. One potential problem with using these values is that they do not take account of the potential interaction of the pollutants present (or the mobility of the pollutants within the sediment) and therefore may underestimate (or even over estimate) the toxicity of the sediment. These guidelines were developed as a method of predicting potential threats to aquatic life from pollution. The Probably Effects Limit (PEL) is the concentration at which adverse effects to aquatic life are most likely to occur and for the CSQG this means that above this value there is a 42% of effects occurring. CSQG are conservative in nature, possibly overestimating the threat to aquatic life, but are seen as a valuable method of predicting the potential for pollution impact in an area. They can be divided into three outcomes; below the TEL (Threshold level) – adverse reaction are rare; between the TEL and PEL – adverse effects occasionally occur; above the PEL – adverse reaction are occur at a statistically significant level.

The concentrations of all pollutants except for Cu, Cr and Total PCB at Speke are above those recommended by the Sediment Quality Guidelines and most of those are above levels thought to cause toxic effects to aquatic organisms. The concentrations for Oglet Bay are also high, indicating that all of these cores are polluted and that for many of the contaminants the levels are high enough to potentially cause toxic effects to the biota and therefore possible be a health risk for humans consuming any aquatic organisms that may bioaccumulate these pollutants.

Collinge *et al.* (1996) showed potentially dangerous concentrations of metals in some fish caught in the Mersey in 1995; ~2mg/kg for Hg in eels (European Quality Standard = 0.3mg/kg), 13 mg/kg As in dab (recommended 1.0mg/kg), Pb in eels ~2mg/kg (recommended 2mg/kg) and many of these fish are taken home by the anglers to be eaten (Personal observation).

Substance	Sediment Quality Guidelines (TEL)	Probable Effect level	Maximum Recorded Value Speke	Most recent value Speke
Arsenic	5.9 mg/kg	17.0 mg/kg	41.7 mg/kg	19.7 mg/kg
Cadmium	0.6 mg/kg	3.5 mg/kg	6.65 mg/kg	1.68 mg/kg
Chromium	37.3 mg/kg	90.0 mg/kg	71 mg/kg	52 mg/kg
Copper	35.7 mg-/kg	197 mg/kg	205 mg/kg	128 mg/kg
Lead	35.0 mg/kg	91.3 mg/kg	515 mg/kg	336 mg/kg
Mercury	0.17 mg/kg	0.486 mg/kg	0.94 mg/kg	0.59 mg/kg
Total PCBs	34.1 µg/kg	277 µg/kg	5.191302 µg/kg	2.068724 µg/kg
Acenaphthene	6.71 µg/kg ‡	88.9 µg/kg §	9618.367 µg/kg	1808.63 µg/kg
Anthracene	46.9 µg/kg ‡	245 µg/kg §	9717.931 µg/kg	4258.015 µg/kg
Benz*(a)*anthracene	31.7 µg/kg	385 µg/kg	606233.8 µg/kg	205589.1 µg/kg
Benzo*(a)*pyrene	31.9 µg/kg	782 µg/kg	905010.4 µg/kg	304440.7 µg/kg
Chrysene	57.1 µg/kg	862 µgkg	417008.8 µg/kg	159578.5 µg/kg
Dibenz*(a,h)*anthracene	6.22 µg/kg ‡	135 µg/kg §	270943.1 µg/kg	73494.5 µg/kg
Fluoranthene	111 µg/kg	2355 µg/kg	451744.1 µg/kg	219306.2 µg/kg
Fluorene	21.2 µg/kg ‡	144 µg/kg §	6118.328 µg/kg	3764.309 µg/kg
Phenanthrene	41.9 µg/kg	515 µg/kg	47925.35 µg/kg	26993.32 µg/kg
Pyrene	53.0 µg/kg	875 µg/kg	375669.7 µg/kg	189829.7 µg/kg
Zinc	123 mg/kg	315 mg/kg	1538 mg/kg	512 mg/kg

‡ Provisional adoption of Marine ISQCs § Provisional adoption of Marine ISQCs

Table 5: Freshwater Sediment Quality Guidelines comparing the Speke Hall core with the recommended concentrations.

Substance	Sediment Quality Guidelines	Probable Effect level	Maximum Recorded Value Upper Marsh	Most recent value Upper Marsh	Maximum Recorded Channel Core	Most recent value Channel Core
Cadmium	0.7 mg/kg	4.2 mg/kg	2.67 mg/kg	0.33 mg/kg	1.72 mg/kg	0.518 mg/kg
Lead	30.2 mg/kg	112 mg/kg	316.89 mg/kg	146.75 mg/kg	227.84 mg/kg	126.29 mg/kg
Mercury	0.13 mg/kg	0.70 mg/kg	14.67 mg/kg	2.72 mg/kg	1.96 mg/kg	0.39 mg/kg
Total PCBs	21.5 µg/kg	189 µg/kg	95.52 µg/kg	38.0 µg/kg	NA	NA
Acenaphthene	6.71 µg/kg	88.9 µg/kg	201.09 µg/kg	17.35 µg/kg	NA	NA
Anthracene	46.9 µg/kg	245 µg/kg	481.01 µg/kg	251.60 µg/kg	NA	NA
Benz*(a)*anthracene	74.8 µg/kg	693 µg/kg	5105.27 µg/kg	1476.28 µg/kg	NA	NA
Benzo*(a)*pyrene	88.8 µg/kg	763 µg/kg	7233.95 µg/kg	2907.29 µg/kg	NA	NA
Chrysene	108 µg/kg	846 µg/kg	11364.44 µg/kg	923.43 µg/kg	NA	NA
Dibenz*(a,h)*anthracene	6.22 µg/kg	135 µg/kg	1798.13 µg/kg	841.78 µg/kg	NA	NA
Fluoranthene	113 µg/kg	1494µg/kg	5210.07 µg/kg	446.29 µg/kg	NA	NA
Fluorene	21.2 µg/kg	144 µg/kg	164.86 µg/kg	17.22 µg/kg	NA	NA
Phenanthrene	86.7 µg/kg	544 µg/kg	2184.35 µg/kg	582.09 µg/kg	NA	NA
Pyrene	153 µg/kg	1398µg/kg	4998.13 µg/kg	637.79 µg/kg	NA	NA
Zinc	124 mg/kg	271 mg/kg	747.49 mg/kg	321.22 mg/kg	550.58 mg/kg	328.72 mg/kg

Table 6: Marine Sediment Quality Guidelines comparing the Oglet Bay cores with the recommended concentrations based on dry weight concentration. Probable effect levels (PELs; dry weight). PEL is the concentration above which the sediments are shown to have statistically significance adverse effects on the benthic biota.

substance	residential with plant uptake	residential without plant uptake	allotments	commercial/ industrial	Upper Marsh Recent	Channel Recent	Speke Recent
Lead	450	450	450	750	146.75	126.29	336
Mercury	8	15	8	480	2.72	0.39	0.59
Cadmium	1,2,8 (for pH 6,7,8)	30	1,2,8 (for pH 6,7,8)	1400	0.33	0.518	1.68

Table 7: Soil guideline values (mg/kg) (Residential with plant uptake is used for all properties with back gardens; Residential without plant uptake is used for all properties with communal gardens or no garden areas; Since there is no soil guideline value for open spaces, residential without plant uptake is commonly used).

Soil Guideline Values (Table 7) were developed by the Environment Agency, using human toxicology data, to give an indication of the potential risk to human health from exposure to a number of pollutants. Different concentrations are given for different land types partially due to the differing uses and users of the land. For example, children are more likely to be exposed in residential areas. If we consider the concentrations found in the various cores from the point of view of potential threat to human health then only the levels of cadmium found at Speke are a potential cause for concern. So whilst it is apparent from the data that there is a potential toxicological threat to aquatic organisms in the area, it would appear there is little danger to the human population from direct exposure to the sediment. However, if aquatic organisms have the tendency to bioaccumulate these pollutants and end up in the human food chain, then there is the potential for human toxicological impact, for example recreational fishermen from New Brighton, who take their catch home to eat, could be in danger.

Metal concentration is often used to assess the contamination levels of the environment however Kraepiel *et al.* (1997) have shown a lack of correlation between concentrations and toxicity, suggesting in fact that the speciation of the metals is more important than the total concentration. Metals that show a positive correlation with organic matter are likely to be strongly bound to the sediment and therefore less bioavailable (Lu *et al.*, 2005). Kirby *et al.* (1998) showed that although contaminants might not be present at acutely toxic levels they could be responsible in lower concentrations for chronic toxicity.

11.3 Pollutant and Disease Interactions

Unfortunately this study did not show any relationship between the levels of pollutants in the sediment cores and selected disease incidence on Merseyside (see appendix for disease data). It is likely that because of the complexity of the factors potentially responsible for disease in Merseyside, the statistical method used was not sensitive enough to identify causative relationships between pollution and health. There are a number of valid reasons why this could be, even when many of the pollutants being investigated have been shown to cause a variety of diseases and are present in the sediment in relatively high concentrations.

1. Pollutants rarely occur singly, therefore any health effects could be the result of a combination of factors rather than down to just one individual contaminant. This means that it can be incredibly difficult to identify which combination is responsible for a particular disease. Even if one particular pollutant is not directly responsible for a disease, it may enhance the effects of others, either by putting the body under stress or by pre-conditioning an organism to respond to another pollutant. The large variety of chemicals being emitted to the environment and the number of sources of these chemicals (Table 8) in the Merseyside area could account for the lack of any obvious cause and effect relationship between pollution and health in the area. The complexity of interaction between these chemicals and those that the population are exposed to on a daily basis from domestic and work sources, e.g. additives in food, chemicals at work, chemicals in toiletries and cosmetics, further complicates the issue.

2. There is the possibility of a time-lag effect, i.e. a disease response to pollution could take a number of years to manifest itself within the population (e.g. smoking can take around 20 years to cause a disease response), or it could require a number of years of chronic low level exposure to initiate a disease response. As the data for cancer incidence only covered a relatively short period, it is possible that the time lag effect was not picked up.

3. Any relationship between disease incidence and pollution is being masked out by other local factors such as population movement, socio-economic levels of deprivation and other causes of disease, e.g. poor diet, lack of exercise, obesity, smoking etc. As there was no provision of patient history, it was impossible to eliminate cases that may have been caused by occupational exposure rather than by a general environmental exposure to potential causative agents.

Examples of discharges to the Merseyside Environment	
Discharges to the atmosphere	**Discharges to rivers and estuaries**
Acetaldehyde (Ethanal), Benzene, Butadiene (1,3-Butadiene), Carbon dioxide, Carbon disulphide, Carbon monoxide, Carbon tetrachloride, Chloroform (Trichloromethane), Ethylene (Ethene), Ethylene dichloride, Formaldehyde (Methanal), Methane, Methylene chloride, Phenol, 1,1,2,2-Tetrachloroethane, Tetrachloroethylene, Toluene, Trichlorobenzene - ll iIsomers, Trichloroethylene, Vinyl chloride, Xylene (All Isomers), Dioxins and furans - as ITEQ, Hydrogen chloride, CFCs, Pentane, Benzyl chloride, Halons (total), HFCs (total), PM10, HCFCs, p-Dichlorobenzene, Benzo(a)Pyrene, Butene - all isomers, Ethyl Toluene - all isomers, Pentene - all isomers, PFCs (total), Trimethylbenzene - all isomers, Nitrogen oxides (as NO2), Hexachlorocyclohexane, Inorganic chlorine compounds, Inorganic fluorine compounds, VOCs (NMVOCs)	Aniline (Benzeneamine) Chlorides, Fluorides, Permethrin, Nonylphenols, Nonylphenol ethoxylates, Octylphenols, Propetamphos, Benzyl butyl phthalate (BBP), Bisphenol-A, DEHP, Diuron, Halogenated organic compounds, Isoproturon, Nitrogen - as total N, Phosphorus - as total P, SCCPs (C10-13), Total organic carbon, Clotrimazole, Perfluoro octanyl sulphate, Triclosan, Asbestos, Aldrin, Arsenic, Atrazine, Azinphos-methyl, Benzene, Cadmium, Carbon tetrachloride, Chloroform (Trichloromethane), Chromium, Copper, DDT - all isomers, Dichlorvos, Dieldrin, Endosulfan, Endrin, Ethylene dichloride, Fenitrothion, Hexachlorobenzene, Hexachlorobutadiene, Lead, Malathion, Mercury, Naphthalene, Nickel, Pentachlorophenol & compounds, PCBs, Simazine, Tetrachloroethylene, Toluene, Trichlorobenzene - ll iIsomers, Methyl chloroform, Trichloroethylene, Trifluralin, Xylene (All Isomers), Zinc, Permethrin, Nonylphenols, Diazinon, Linuron, Dimethoate, Chlorfenvinphos, 1,1,2-Trichloroethane, 2-Chlorophenol, 2,4 D (Ester), 2,4 D (Non-Ester), 2,4-Dichlorophenol, 4-Chloro-3-methylphenol, Azinphos-ethyl, Bentazone, Biphenyl, Chloronitrotoluenes, Demeton, Fenthion, Isodrin, Mecoprop, Mevinphos, Nonylphenol ethoxylates, Octylphenols, Omethoate, Parathion, Parathion methyl, Triazophos, Tributyltin compounds, Triphenyltin compounds, Hexachlorocyclohexane

Table 8: A small sample of the chemicals being discharged to the Merseyside area under permit. There are over 200 companies licensed to discharge a wide variety of chemicals both into the local rivers and estuary and into the atmosphere.

4. The levels of pollutants in the sediment could have been concentrated due to diagenetic remobilisation and, therefore, overestimate the levels of pollutants the local population are exposed to. Any resuspension and remobilisation occurring

could mean that the concentrations in the sediment are not representative of the chronological release and deposition of the contaminants.

5. Pollutant concentrations in the sediment are not necessarily representative of the levels that the local population are exposed to, due to differing pathways of exposure. For example, Hg could enter the environment *via* direct discharge to the river and, therefore, bypass the local population to whom the most important route of exposure might be inhalation from atmospheric discharges.

The assumption made in comparing the pollution data with the health data, is that the majority of human exposure in the Merseyside area is *via* inhalation. If this is the case, then the core taken at Speke Hall would be a better indicator of the potential for the contaminants to cause health problems, as the majority of pollutants measured in it will have come *via* atmospheric sources.

11.4 Prevailing Wind Data

The wind rose for Speke (Fig 63a) indicates that the prevailing winds for the area are from the west and the south, with the strongest winds coming from the west and the north west. The prevailing winds for Manchester (Fig 63b) are predominately from the south and west and, in general, are not as strong as those measured at Speke.

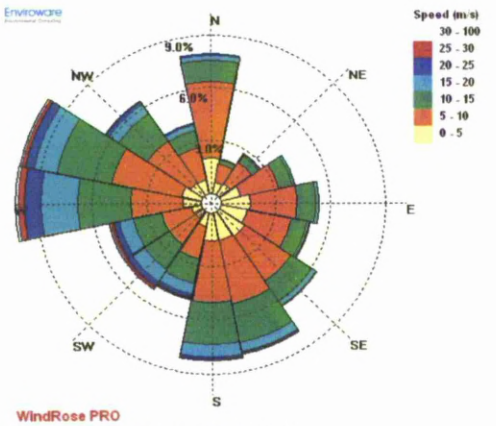


Figure 63a: Speke Wind Rose. Prevailng wind speed and direction from 1969 to 1998.

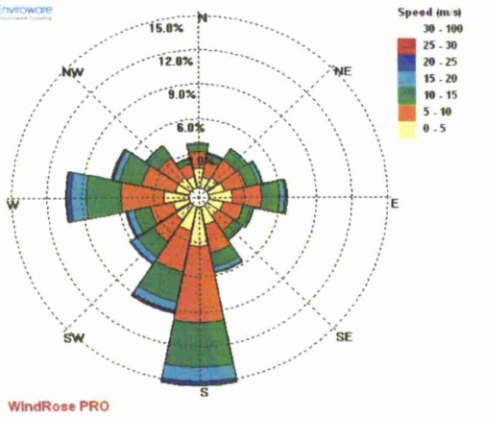


Figure 63b: Manchester Wind Rose. Prevailing wind speed and direction from 1949 to 1995.

The differences in wind strength and direction are probably due to the Speke location being near the coast and, therefore, subjected more to the influence of the Irish Sea. The wind direction would point to atmospheric sources of local pollution being from the Wirral and Ellesmere Port areas with some input from the St Helens, Warrington and Runcorn areas as well. All these locations have a long history of industry and in particular an association with the chemical industry which could help in explaining the variety of pollutants (heavy metals, PCBs and PAHs) found in this study. The strength of the wind from the Irish Sea area could point to long range sources of atmospheric pollution also being involved.

11.5 Chapter Summary

Although there are similar processes (sediment source and sedimentation rate, lithogenic control, grain size factors, organic matter content, diagenesis, pollution input, desorption) influencing the cores, the mechanisms by which these act will vary between environments. This can be seen from the variation in metal concentrations and correlations, the grain size differences, the amount of organic matter and pollutants present in the cores from the different locations. The less dynamic nature of the environment would suggest that a core from an isolated lake is less disturbed so would provide a more complete record of atmospheric pollution. It would seem that the majority of pollutants enter the Speke core from atmospheric sources, whilst the estuarine cores receive most of their pollutant input from aquatic sources.

CHAPTER 12
CONCLUSIONS AND FURTHER WORK

12.1 Conclusions

A number of aims for the research conducted in this thesis were suggested in Chapter One and several hypotheses were proposed to assist in investigating these aims; whether or not the data collected supports or refutes these hypotheses is discussed in the following text.

The first aim of this study was to investigate historic pollution in saltmarsh, intertidal and lake sediment cores taken from the South Liverpool area. This was done by taking cores from a saltmarsh and an intertidal area (both in Oglet Bay in the Mersey Estuary) and a lake at Speke Hall. The data collected from these locations supported the first hypothesis that the Mersey Estuary is a historically polluted ecosystem, and although levels of pollution have improved in recent years, concentrations of the main pollutants (Pb, Zn, Hg, Cd, PCBs and PAHs) are above the background levels that guideline values (CSQG) consider to be potentially dangerous to aquatic organisms. However, with the exception of Cd at Speke, none of the metals are present at a concentration that would be considered dangerous to human health. Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) are still present in concentrations that are considered to pose potential health problems for aquatic organisms and the local human population.

Environmental pollution in the Merseyside area is indicated by the levels of metals (in particular Pb and Zn) that have been recorded in estuary and lake sediment cores that are above background levels, and by the relatively high concentrations of organic pollutants (PCBs and PAHs) that were found in the sediment. The reduction in the levels of metal pollutants (Pb, Cd and Zn in particular) near the surface of the cores suggests that the Mersey area has become cleaner in recent years. This could possibly be due to a combination of stricter government regulations on discharge levels, companies using cleaner technologies which limit the pollutants produced and a decline in the amount of industrial activity in the region. However, the reduction in Pb levels towards the surface of the cores could also be related to the reduction in the

use of leaded petrol in recent years, or it may reflect other factors within the sediment core; such as a variation in particle size throughout the core or diagenetic processes occurring deeper in the sediment.

The organic pollutants do not exhibit the same trends of decreasing concentration towards the surface of the cores as the metals. This could be due to a number of reasons. Organic pollutants (PCBs and PAHs) have a wide variety of sources, including natural processes (vegetation burning), legitimate industrial releases and accidental releases from spillages. Many of the industrial sources have changed over the years, due to new industries moving to the area, old industries declining and closing and new technologies leading to new processes and, therefore, new sources/types of pollutant input. All these factors contribute to a great deal of variety in the mix of pollutants and concentrations entering the environment. POPs are resistant to degradation, which means they persist in the environment for many years and this could have a smoothing influence on their concentrations, due to factors like their potential for storage in sediment and remobilisation (a process which could happen multiple times). The lack of a trend in sediment concentrations could also be partially explained by old equipment being decommissioned and placed in landfill, leading to the release of the contaminants contained within this equipment as it degrades, or the increase in road traffic, change in population density and change in industrial processes in the region over the last 50 years or even other unknown factors that do not appear to have a direct or specific link. The wide variety of industry in the Merseyside area means that trends in organic pollution input to the region and sources of these pollutants are probably masked by the number of sources (local, national and, potentially, international) emitting these substances over the years.

The second aim of this study was to attempt to distinguish different pollutant transport pathways between cores from a lake and the intertidal zone. The hypothesis is that there exists a difference in the sources and transport pathways of pollutants reaching sediment cores from different environments (lake, saltmarsh and sand bank); the lake core is likely to receive most of its pollutants via atmospheric sources whilst the intertidal zone will receive predominantly waterborne pollution. The differences in pollutant concentrations and profiles between the three cores can

potentially be explained by the different sources of these pollutants. The data suggest that the majority of pollution entering the Speke Hall lake site is from atmospheric sources, whilst the Oglet Bay sites receive a mixture of waterborne and atmospheric contaminants. The fact that PAH concentrations are higher at Speke Hall suggests that the majority of inputs of these are from industrial and vehicular sources *via* atmospheric deposition. Lower levels are found in Oglet Bay, as the more dynamic nature of the environment here and the influx of relatively uncontaminated marine sediment have a diluting effect on PAH concentrations. PCB concentrations are higher in the estuarine core than the lake core, suggesting that in the Merseyside area PCBs are primarily entering the environment from waterborne estuarine sources.

The differences in organic matter content and sediment grain sizes between the cores can be explained by local factors acting on inputs to the sediment. The organic matter present in the upper part of the Upper Marsh core is likely to be related to colonisation of the marsh by vegetation, whilst the very high levels of organic matter found at Speke Hall are due to the lake being surrounded by woodland and associated lake margin vegetation. The grain size of the organic matter at Speke Hall was predominantly in the sand grade. This could have been due to the high levels of organic matter present, to high levels of surface wash bringing in coarse grained organic sediment or to a combination of these two factors.

A third research aim focused on the viability of using sediment cores from different locations (saltmarsh, intertidal sand bank and lake) as a method of identifying historical pollution inputs to a region, which are dependent on the level of disturbance at a site and the pathways the pollutants take to reach the sediment. The Channel core is in a more dynamic environment than the Upper Marsh core and it is likely that any trends in pollution that could be detected have been smoothed by the nature of the processes taking place in the core location: high frequency working of the sediment before it enters the sediment record meaning, in essence, that the source to sink processing time is lengthened in this high energy environment. This means that a core from a dynamic setting is much less useful for determining the pollution history of an area than a core from a stable depositional environment. From the data acquired for this project it would appear that the core from the Speke Hall Lake location provides a more accurate record of the pollution history of the area than

those from the more dynamic saltmarsh environment. Although if certain pollutants (e.g. PCBs) are more likely to be transported *via* estuarine routes, then a core from an area receiving predominantly airborne pollution (like that taken at Speke Hall) could under-represent the environmental concentrations of these pollutants.

If the assumption is made that the majority of human exposure to pollutants is *via* inhalation of airborne particulates, then the core from Speke Hall lake would be a better core to use to assess potential health impacts of pollutants. Concentrations of most metals and PAHs are higher at Speke Hall pond which would suggest an airborne source, whilst PCBs and Hg are higher in the estuary core, which would suggest that their source is predominantly aquatic in nature.

The final aim of the thesis was to assess (as a discussion point) the potential viability of using the historical pollution record from sediment cores as a method of identifying and explaining pollution-related health issues in local populations. The ability to do this would be dependent on various factors including; local population dynamics, the continuity of the pollution record and the level of detail available in the health records available for a region. Unfortunately, due to the nature of the health data acquired for this project and the complexity in linking environmental pollution to health in both time and space, it has not been possible to show a relationship between the historic pollutant inputs to the region (as recorded by sediment cores) and the disease data. However, this does not mean that the industrial history of Merseyside has had no influence on public health; it simply means that more detailed investigation is necessary and the possibility that pollution is responsible for at least some of the high levels of disease in the area should not be ignored.

The failure to examine any link between the historical pollution input to the region and disease incidence illustrates the complexity of the factors involved in pollution-related disease incidence (local population dynamics, the continuity of the pollution record and the level of detail in the health records available for a region). With the health data obtained for this study, it is unlikely that a link between the pollution history of the region and disease incidence could have been found. The number of factors involved in generating disease incidence and the pollution record mean that a

statistically significant correlation was unlikely to be achieved. The data from the cores was from such a wide range of sources and large catchment area (including, but not limited to, the Mersey Basin and Manchester) that any local factors were potentially masked by input from the area as a whole. There was also the problem of spatial and temporal incompatibility between the data sets. The time period covered by the cores is different from that of the health data and, with the small number of cores taken, a spatial relationship would have been difficult to prove. For a future study of this kind to work, much more comprehensive data sets would be required, including cores from a much greater number of sample sites in the region, more temporal resolution of the data from the cores and much more detailed health and sociological data. Even then, generating a link between the data sets could be incredibly difficult, if not impossible.

One of the limiting factors in this study is a lack of appropriate dating (e.g. ^{210}Pb) of any of the sediment cores. An attempt to date the lake core has been made by comparing the Speke Hall core to cores taken by other workers at the same site (Worsley, 2005; Power, 2009). This comparison suggests that the core from the present study is approximately 70 years old and is not deep enough to include the natural background levels of elements (the PCBs in the lower parts of the core support this theory, as they only began to appear in the sediment record in the 1930s). An attempt to date the Upper Marsh core by using the Pb profile suggested that the increase in Pb concentration up-core from 60 cm depth possibly corresponds to the increasing use of motor vehicles from the 1950s onwards. However, both of these dating methods have the potential to be incorrect due to the fluctuating nature of pollutant input to the sediment, the potential for disturbance and remobilisation of the contaminants, and fluctuating sedimentation rates that can occur in the system. However, the strengths of the research presented in this thesis are both the comparisons it makes between lake and estuarine cores and the wide range of organic and inorganic constituents analysed using identical techniques.

The study is unable to demonstrate a link between the pollution history of the region and the regional health data available, due the uncertainties in the pollution history reconstruction that was possible and complexity of factors involved in disease incidence.

12.2 Further Work

There are a number of research avenues that must be pursued to fully investigate some of the issues revealed in the present study.

To establish a better temporal resolution of the pollution record, ^{210}Pb dating of the sediment cores from all locations could be undertaken. This would enable a more accurate comparison of trends and deposition rates between the cores, it would allow an attempt to link up particular pollutants with known releases to the local environment e.g. PAHs with the Mersey Oil spill in 1989, and also an attempt to be made to see if there is a noticeable relationship between pollutant concentrations in the sediment and the introduction of government regulations/policy changes, e.g. the reduction in Pb concentrations with the introduction of unleaded petrol. It would also help with the attempt to link the pollution record to the health data by giving more accurate information about the variations in pollutant input to the system over the years and allow for the consideration of any time lag effects between the local pollution and any health effects. However, even with a better temporal resolution it is unlikely that a significant link between the pollutions and the health data would be found (due to the reasons discussed in the previous section).

A more detailed investigation of the variety of pollutant inputs from the local environment could be conducted, expanding the range to include more organic pollutants, for example those that make up the United Nations Environment Programme Governing Council 'Dirty Dozen': aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, PCBs, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and toxaphene and possibly polybrominated flame retardants and organometal compounds such as TBT.

A larger scale study could be conducted investigating more lakes in the area, for example to allow comparison of lakes in more developed parts of the Mersey Basin, e.g. Speke Hall, with lakes in less developed locations, e.g. Rostherne Mere in Cheshire (it should be noted, however, that although Rostherne Mere is in a more rural location than Speke Hall, it is situated next to the M56 motorway which could

influence the variety and amounts of pollutants entering the lake sediment). The effects of the estuarine currents on pollutant dispersion could be investigated by undertaking a more extensive survey of the estuary, covering locations both upstream and downstream from Oglet Bay, on both sides of the estuary, to see whether there are any locations where sediments and, therefore, pollutants are being concentrated due to water circulation. This survey could also be expanded to include other estuaries within the Mersey Basin, e.g. the Ribble and the Dee, to assess the differences in pollution input in different parts of the region and compare more urbanised locations with more rural locations. A study like this would require a large amount of funding and might be better conducted as a number of smaller projects (e.g. PhDs). Each of these could be focused on a smaller area, with the overall methodology standardised between projects to allow for the data to be combined once the individual studies were completed.

A study investigating the potential bioavailability of the pollutants could be undertaken. It would be interesting to look at the whether or not these pollutants are found in the ultrafine respirable particle size fraction, which has the potential to cause numerous health problems when inhaled. More detailed particle size analysis could be carried out to investigate what particle size the most pollution is found on and see if it is the smaller grain size fraction. If there are high concentrations of contaminants on respirable particles sizes then remobilisation of these particle sizes could be a potential health hazard to people living near areas with sediments containing high concentrations of pollutants. This study could also examine metal speciation within the sediment, in order to identify those metals which are more likely to be remobilised by diagenetic processes, sediment resuspension or bioturbation and which, therefore, are a potential health hazard to aquatic organisms or the local human population.

The collection of more detailed health records (e.g. patient histories) for disease incidence for the region would allow an attempt to be made to eliminate genetic and socio-economic factors from the investigation and the development of a more comprehensive picture of factors affecting disease incidence in Merseyside. As part of this data acquisition, the collection of long-term data sets for disease incidence in the area could be undertaken. This would be a complicated process due to the

potential time-lag between exposure, onset of disease and population flux in the area. The mode of exposure (inhalation, transdermal, ingestion) would affect these issues, as would the change in the level of population mobility in recent years. The varying nature of pollution input to the region and the variety of sources, both local and long range, would also have an impact on the ability to correlate disease incidence and historical pollution releases in the region. In order to try to link pollution with disease incidence, a variety of other long term data sets would be needed and would include data on the movement of people into and out of the region, data on sources of pollution both local and regional, and any potential long range sources and data on the various pathways that pollutants would take to arrive in the region (e.g. wind direction).

It is likely that, with the wide variety and complexity of data needed to examine possible links between the pollution history and disease incidence in the region, it is an unrealistic goal to set. A more feasible approach would be to concentrate on selected, fewer pollutants or on diseases with known pollutant links.

APPENDIX 1

This Appendix contains summary tables of the Pearson Product Moment Correlation Co-efficient values for all the parameters tested for each of the three cores investigated. They are listed in the same order that that the cores are treated in the main text of this thesis: Upper Marsh Core, Channel Core and Speke Hall Lake Core.

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
P C	Si	1.00	**0.714****	0.441**	**0.763****	-0.260*	-0.605**	-0.248*	-0.07	**-0.716****	0.00	0.13	-0.636**	**0.834****	-0.533**	0.09	-0.20	-0.242*	-0.13	-0.386**	0.299*	0.07
S			**0.00**	0.00	**0.00**	0.03	0.00	0.04	0.58	**0.00**	0.97	0.30	0.00	**0.00**	0.00	0.45	0.10	0.05	0.30	0.00	0.01	0.59
P C	Al	**0.714****	1.00	0.323**	0.657**	0.00	-0.525**	-0.292*	0.12	-0.346**	0.22	0.272*	-0.605**	0.563**	-0.312**	0.06	-0.04	-0.321**	-0.14	-0.17	0.286*	0.19
S		**0.00**		0.01	0.00	0.98	0.00	0.02	0.35	0.00	0.08	0.02	0.00	0.00	0.01	0.65	0.73	0.01	0.26	0.17	0.02	0.13
P C	Ti	0.441**	0.323**	1.00	0.341**	0.445**	-0.06	-0.13	-0.03	-0.23	0.03	0.05	-0.295*	0.419**	-0.359**	0.01	0.02	-0.13	0.21	-0.539**	0.241*	0.01
S		0.00	0.01		0.00	0.00	0.63	0.30	0.80	0.06	0.80	0.66	0.01	0.00	0.00	0.95	0.87	0.29	0.08	0.00	0.05	0.96
PC	Ca	**0.763****	0.657**	0.341**	1.00	0.07	-0.479**	-0.522**	0.401**	-0.321**	0.450**	0.547**	**-.0835****	0.589**	-0.301*	0.459**	-0.317**	-0.16	-0.11	-0.09	0.477**	0.362**
S		**0.00**	0.00	0.00		0.57	0.00	0.00	0.00	0.01	0.00	0.00	**0.00**	0.00	0.01	0.00	0.01	0.21	0.36	0.49	0.00	0.00
PC	K	-0.260*	0.00	0.445**	0.07	1.00	0.414**	-0.16	0.351**	0.437**	0.277*	0.265*	-0.05	-0.356**	0.258*	0.13	0.11	-0.08	0.23	0.04	0.09	0.16
S		0.03	0.98	0.00	0.57		0.00	0.20	0.00	0.00	0.02	0.03	0.69	0.00	0.03	0.30	0.35	0.54	0.06	0.72	0.46	0.20
PC	Fe	-0.605**	-0.525**	-0.06	-0.479**	0.414**	1.00	0.484**	0.16	0.498**	0.03	-0.08	0.497**	-0.641**	0.17	0.20	0.243*	0.15	0.03	0.07	-0.22	-0.02
S		0.00	0.00	0.63	0.00	0.00		0.00	0.20	0.00	0.84	0.50	0.00	0.00	0.18	0.11	0.05	0.23	0.79	0.56	0.07	0.86
PC	Mn	-0.248*	-0.292*	-0.13	-0.522**	-0.16	0.484**	1.00	-0.17	0.08	-0.12	-0.20	0.508**	-0.288*	0.02	-0.07	0.21	0.07	0.01	-0.15	-0.275*	-0.15
S		0.04	0.02	0.30	0.00	0.20	0.00		0.17	0.51	0.31	0.10	0.00	0.02	0.89	0.58	0.09	0.57	0.96	0.22	0.02	0.21
PC	S	-0.07	0.12	-0.03	0.401**	0.351**	0.16	-0.17	1.00	0.446**	0.678**	0.617**	-0.335**	-0.15	0.14	0.384**	0.08	0.02	-0.06	0.244*	0.433**	0.317**
S		0.58	0.35	0.80	0.00	0.00	0.20	0.17		0.00	0.00	0.00	0.01	0.23	0.27	0.00	0.51	0.86	0.64	0.04	0.00	0.01
PC	Cl	**-0.716****	-0.346**	-0.23	-0.321**	0.437**	0.498**	0.08	0.446**	1.00	0.239*	0.14	0.361**	-0.678**	0.422**	0.16	0.269*	0.251*	0.09	0.499**	-0.11	0.07
S		**0.00**	0.00	0.06	0.01	0.00	0.00	0.51	0.00		0.05	0.27	0.00	0.00	0.00	0.18	0.03	0.04	0.46	0.00	0.38	0.56
PC	Pb	0.00	0.22	0.03	0.450**	0.277*	0.03	-0.12	0.678**	0.239*	1.00	**0.901****	-0.521**	-0.08	0.15	0.428**	0.03	-0.15	-0.10	0.10	0.550**	0.576**
S		0.97	0.08	0.80	0.00	0.02	0.84	0.31	0.00	0.05		**0.00**	0.00	0.50	0.24	0.00	0.79	0.24	0.43	0.43	0.00	0.00
PC	Zn	0.13	0.272*	0.05	0.547**	0.265*	-0.08	-0.20	0.617**	0.14	**0.901****	1.00	-0.622**	0.01	0.12	0.366**	-0.10	-0.17	-0.16	0.04	0.641**	0.647**
S		0.30	0.02	0.66	0.00	0.03	0.50	0.10	0.00	0.27	**0.00**		0.00	0.94	0.31	0.00	0.42	0.17	0.20	0.74	0.00	0.00
P C	Br	-0.636**	-0.605**	-0.295*	**-0.835****	-0.05	0.497**	0.508**	-0.335**	0.361**	-0.521**	-0.622**	1.00	-0.598**	0.298*	-0.23	0.22	0.350**	0.13	0.17	-0.651**	-0.421**
S		0.00	0.00	0.01	**0.00**	0.69	0.00	0.00	0.01	0.00	0.00	0.00		0.00	0.01	0.06	0.08	0.00	0.28	0.16	0.00	0.00
PC	Zr	**0.834****	0.563**	0.419**	0.589**	-0.356**	-0.641**	-0.288*	-0.15	-0.678**	-0.08	0.01	-0.598**	1.00	-0.452**	-0.06	-0.17	-0.323**	-0.07	-0.463**	0.248*	-0.10
S		**0.00**	0.00	0.00	0.00	0.00	0.00	0.02	0.23	0.00	0.50	0.94	0.00		0.00	0.62	0.16	0.01	0.58	0.00	0.04	0.43
PC	Rb	-0.533**	-0.312**	-0.359**	-0.301*	0.258*	0.17	0.02	0.14	0.422**	0.15	0.12	0.298*	-0.452**	1.00	-0.20	0.15	0.05	0.24	0.251*	-0.12	0.03
S		0.00	0.01	0.00	0.01	0.03	0.18	0.89	0.27	0.00	0.24	0.31	0.01	0.00		0.10	0.22	0.69	0.05	0.04	0.32	0.81
PC	Sr	0.09	0.06	0.01	0.459**	0.13	0.20	-0.07	0.384**	0.16	0.428**	0.366**	-0.23	-0.06	-0.20	1.00	-0.18	0.15	-0.393**	0.353**	0.00	0.267*
S		0.45	0.65	0.95	0.00	0.30	0.11	0.58	0.00	0.18	0.00	0.00	0.06	0.62	0.10		0.14	0.22	0.00	0.00	0.98	0.03
P C	Cr	-0.20	-0.04	0.02	-0.317**	0.11	0.243*	0.21	0.08	0.269*	0.03	-0.10	0.22	-0.17	0.15	-0.18	1.00	-0.18	0.01	-0.02	-0.11	-0.10
S		0.10	0.73	0.87	0.01	0.35	0.05	0.09	0.51	0.03	0.79	0.42	0.08	0.16	0.22	0.14		0.15	0.91	0.87	0.37	0.40
PC	Ni	-0.242*	-0.321**	-0.13	-0.16	-0.08	0.15	0.07	0.02	0.251*	-0.15	-0.17	0.350**	-0.323**	0.05	0.15	-0.18	1.00	0.09	0.274*	-0.239*	0.02
S		0.05	0.01	0.29	0.21	0.54	0.23	0.57	0.86	0.04	0.24	0.17	0.00	0.01	0.69	0.22	0.15		0.45	0.02	0.05	0.88
PC	Y	-0.13	-0.14	0.21	-0.11	0.23	0.03	0.01	-0.06	0.09	-0.10	-0.16	0.13	-0.07	0.24	-0.393**	0.01	0.09	1.00	-0.14	-0.06	-0.15
S		0.30	0.26	0.08	0.36	0.06	0.79	0.96	0.64	0.46	0.43	0.20	0.28	0.58	0.05	0.00	0.91	0.45		0.27	0.63	0.22
P C	LOI	-0.386**	-0.17	-0.539**	-0.09	0.04	0.07	-0.15	0.244*	0.499**	0.10	0.04	0.17	-0.463**	0.251*	0.353**	-0.02	0.274*	-0.14	1.00	-0.356**	0.09
S		0.00	0.17	0.00	0.49	0.72	0.56	0.22	0.04	0.00	0.43	0.74	0.16	0.00	0.04	0.00	0.87	0.02	0.27		0.00	0.47
PC	Cd	0.299*	0.286*	0.241*	0.477**	0.09	-0.22	-0.275*	0.433**	-0.11	0.550**	0.641**	-0.651**	0.248*	-0.12	0.00	-0.11	-0.239*	-0.06	-0.356**	1.00	0.443**
S		0.01	0.02	0.05	0.00	0.46	0.07	0.02	0.00	0.38	0.00	0.00	0.00	0.04	0.32	0.98	0.37	0.05	0.63	0.00		0.00
P C	Hg	0.07	0.19	0.01	0.362**	0.16	-0.02	-0.15	0.317**	0.07	0.576**	0.647**	-0.421**	-0.10	0.03	0.267*	-0.10	0.02	-0.15	0.09	0.443**	1.00
S		0.59	0.13	0.96	0.00	0.20	0.86	0.21	0.01	0.56	0.00	0.00	0.00	0.43	0.81	0.03	0.40	0.88	0.22	0.47	0.00	

Table 9: Upper Marsh Pearson Product Moment Correlations – Elements versus Elements

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
PC	χ L F	0.602**	0.504**	0.301*	**0.755****	-0.02	-0.286*	-0.15	0.401**	-0.337**	0.699**	**0.770****	**-0.753****	0.457**	-0.246*	0.311**	-0.17	-0.267*	-0.15	-0.324**	0.677**	0.519**
S		0.00	0.00	0.01	**0.00**	0.86	0.02	0.22	0.00	0.00	0.00	**0.00**	**0.00**	0.00	0.04	0.01	0.17	0.03	0.23	0.01	0.00	0.00
PC	F D %	-0.06	-0.02	0.14	-0.09	0.20	0.260*	0.278*	0.00	0.10	0.08	-0.05	0.17	-0.19	0.04	0.12	0.05	0.02	0.10	-0.06	-0.11	-0.06
S		0.65	0.88	0.27	0.49	0.11	0.03	0.02	0.99	0.43	0.54	0.66	0.17	0.13	0.72	0.33	0.66	0.84	0.43	0.65	0.36	0.60
PC	S I R M	0.536**	0.457**	0.248*	**0.716****	0.01	-0.22	-0.14	0.468**	-0.269*	**0.712****	**0.786****	**-0.726****	0.392**	-0.19	0.299*	-0.11	-0.267*	-0.18	-0.284*	0.674**	0.523**
S		0.00	0.00	0.04	**0.00**	0.96	0.07	0.25	0.00	0.03	**0.00**	**0.00**	**0.00**	0.00	0.11	0.01	0.36	0.03	0.15	0.02	0.00	0.00
PC	χARM	0.08	0.03	0.03	0.17	0.13	0.259*	0.269*	0.360**	-0.14	0.554**	0.560**	-0.22	-0.10	0.05	0.12	0.06	-0.20	-0.15	-0.253*	0.389**	0.476**
S		0.52	0.82	0.83	0.16	0.30	0.03	0.03	0.00	0.27	0.00	0.00	0.07	0.42	0.71	0.33	0.65	0.11	0.23	0.04	0.00	0.00
PC	χARM/SIRM	-0.386**	-0.405**	-0.19	-0.503**	0.10	0.556**	0.556**	-0.05	0.01	-0.06	-0.12	0.471**	-0.464**	0.21	-0.19	0.21	-0.02	0.00	-0.11	-0.20	0.03
S		0.00	0.00	0.12	0.00	0.41	0.00	0.00	0.70	0.95	0.63	0.32	0.00	0.00	0.09	0.13	0.08	0.89	0.97	0.37	0.10	0.82
PC	SIRMχLF	-0.17	-0.12	-0.19	-0.04	0.10	0.286*	0.02	0.392**	0.23	0.16	0.21	-0.02	-0.19	0.19	-0.04	0.268*	-0.09	-0.18	0.08	0.15	0.09
S		0.17	0.34	0.12	0.74	0.40	0.02	0.84	0.00	0.06	0.18	0.09	0.85	0.12	0.13	0.77	0.03	0.47	0.14	0.52	0.22	0.47
PC	χARM/χLF	-0.382**	-0.415**	-0.22	-0.486**	0.12	0.580**	0.534**	0.03	0.05	-0.02	-0.07	0.445**	-0.478**	0.239*	-0.18	0.245*	-0.03	-0.02	-0.09	-0.16	0.05
S		0.00	0.00	0.08	0.00	0.35	0.00	0.00	0.81	0.69	0.86	0.55	0.00	0.00	0.05	0.13	0.04	0.81	0.85	0.45	0.19	0.70
PC	H I R M	0.251*	0.328**	0.286*	0.486**	0.21	-0.321**	-0.376**	0.331**	-0.09	0.534**	0.619**	-0.563**	0.18	0.02	0.01	-0.18	0.01	-0.06	-0.15	0.604**	0.524**
S		0.04	0.01	0.02	0.00	0.08	0.01	0.00	0.01	0.49	0.00	0.00	0.00	0.15	0.88	0.97	0.15	0.94	0.62	0.21	0.00	0.00
PC	HARD %	-0.478**	-0.294*	-0.11	-0.517**	0.13	-0.05	-0.15	-0.353**	0.292*	-0.487**	-0.518**	0.475**	-0.344**	0.261*	-0.362**	-0.02	0.363**	0.20	0.292*	-0.418**	-0.285*
S		0.00	0.01	0.36	0.00	0.29	0.66	0.23	0.00	0.02	0.00	0.00	0.00	0.00	0.03	0.00	0.89	0.00	0.11	0.02	0.00	0.02
PC	A R M	0.08	0.03	0.03	0.17	0.13	0.259*	0.269*	0.360**	-0.14	0.554**	0.560**	-0.22	-0.10	0.05	0.12	0.06	-0.20	-0.15	-0.253*	0.389**	0.476**
S		0.52	0.82	0.83	0.16	0.30	0.03	0.03	0.00	0.27	0.00	0.00	0.07	0.42	0.71	0.33	0.65	0.11	0.23	0.04	0.00	0.00
PC	SIRM/ARM	0.362**	0.364**	0.20	0.430**	-0.15	-0.566**	-0.518**	-0.03	-0.04	-0.04	0.03	-0.404**	0.490**	-0.21	0.09	-0.20	0.03	0.02	0.04	0.16	-0.09
S		0.00	0.00	0.10	0.00	0.22	0.00	0.00	0.79	0.73	0.77	0.79	0.00	0.00	0.09	0.44	0.09	0.82	0.85	0.74	0.18	0.46
PC	S o f t	0.583**	0.496**	0.295*	**0.728****	0.00	-0.272*	-0.17	0.442**	-0.272*	0.652**	**0.748****	**-0.746****	0.475**	-0.24	0.289*	-0.09	-0.300**	-0.17	-0.252*	0.649**	0.482**
S		0.00	0.00	0.01	**0.00**	0.97	0.02	0.16	0.00	0.02	0.00	**0.00**	**0.00**	0.00	0.05	0.02	0.47	0.01	0.16	0.04	0.00	0.00
PC	-20mT	0.397**	0.342**	0.23	0.371**	-0.01	-0.263*	-0.16	0.17	-0.13	0.17	0.273*	-0.423**	0.444**	-0.239*	0.12	0.04	-0.23	-0.10	-0.01	0.262*	0.13
S		0.00	0.00	0.06	0.00	0.93	0.03	0.18	0.17	0.27	0.17	0.02	0.00	0.00	0.05	0.34	0.77	0.06	0.44	0.95	0.03	0.28
PC	-300mT	0.478**	0.294*	0.11	0.517**	-0.13	0.05	0.15	0.353**	-0.292*	0.487**	0.518**	-0.475**	0.344**	-0.261*	0.362**	0.02	-0.363**	-0.20	-0.292*	0.418**	0.285*
S		0.00	0.01	0.36	0.00	0.29	0.66	0.23	0.00	0.02	0.00	0.00	0.00	0.00	0.03	0.00	0.89	0.00	0.11	0.02	0.00	0.02

Table 10: Upper Marsh Pearson Product Moment Correlations – Elements versus Magnetics

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
PC	Mean	-0.14	-0.246*	-0.13	-0.546**	-0.364**	0.07	0.344**	-0.496**	-0.01	-0.673**	**-0.748****	**0.690****	-0.07	0.02	-0.322**	0.21	0.16	0.09	-0.04	-0.628**	-0.615**
S		0.24	0.04	0.28	0.00	0.00	0.59	0.00	0.00	0.95	0.00	**0.00**	0.00	0.60	0.85	0.01	0.08	0.20	0.46	0.77	0.00	0.00
PC	Sorting	-0.509**	-0.458**	-0.22	**-0.777****	-0.12	0.362**	0.408**	-0.406**	0.259*	-0.578**	-0.681**	**0.854****	-0.444**	0.22	-0.328**	0.284*	0.21	0.09	0.09	-0.627**	-.0484**
S		0.00	0.00	0.07	**0.00**	0.32	0.00	0.00	0.00	0.03	0.00	0.00	**0.00**	0.00	0.07	0.01	0.02	0.08	0.45	0.47	0.00	0.00
PC	Skewness	**-0.723****	-0.579**	-0.329**	**-0.880****	0.04	0.540**	0.407**	-0.352**	0.409**	-0.502**	-0.593**	**0.887****	-0.652**	0.343**	-0.292*	0.276*	0.23	0.06	0.23	-0.620**	-0.383**
S		**0.00**	0.00	0.01	**0.00**	0.72	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**	0.00	0.00	0.02	0.02	0.06	0.64	0.06	0.00	0.00
PC	Kurtosis	0.446**	0.276*	.293*	0.553**	-0.05	-0.16	-0.245*	0.315**	-0.21	0.320**	0.401**	-0.450**	0.348**	-0.16	0.258*	-0.04	-0.06	-0.19	-0.22	0.462**	0.246*
S		0.00	0.02	0.02	0.00	0.70	0.20	0.04	0.01	0.09	0.01	0.00	0.00	0.00	0.21	0.03	0.72	0.60	0.13	0.07	0.00	0.04
PC	%Sand	-0.371**	-0.355**	-0.21	-0.687**	-0.21	0.23	0.356**	-0.460**	0.17	-0.660**	**-0.779****	**0.789****	-0.276*	0.12	-0.292*	0.257*	0.21	0.07	0.10	-0.693**	-0.596**
S		0.00	0.00	0.09	0.00	0.08	0.06	0.00	0.00	0.17	0.00	**0.00**	**0.00**	0.02	0.33	0.02	0.03	0.08	0.56	0.42	0.00	0.00
PC	%Mud	0.371**	0.355**	0.21	0.687**	0.21	-0.23	-0.356**	0.460**	-0.17	0.660**	**0.779****	**-0.789****	0.276*	-0.12	0.292*	-0.257*	-0.21	-0.07	-0.10	0.693**	0.596**
S		0.00	0.00	0.09	0.00	0.08	0.06	0.00	0.00	0.17	0.00	0.00	0.00	0.02	0.33	0.02	0.03	0.08	0.56	0.42	0.00	0.00
PC	%vcoarse sand	-0.15	-0.275*	-0.12	-0.291*	-0.23	0.05	0.19	-0.12	0.05	-0.16	-0.14	0.439**	-0.09	0.19	-0.318**	-0.03	0.12	0.22	-0.13	-0.13	-0.16
S		0.22	0.02	0.33	0.02	0.06	0.67	0.13	0.32	0.68	0.20	0.25	0.00	0.45	0.12	0.01	0.84	0.33	0.08	0.30	0.31	0.18
PC	%coarse sand	-0.274*	-0.367**	-0.16	-0.592**	-0.260*	0.21	0.384**	-0.353**	0.10	-0.461**	-0.479**	**0.732****	-0.261*	0.20	-0.394**	0.20	0.11	0.15	-0.09	-0.422**	-0.364**
S		0.02	0.00	0.20	0.00	0.03	0.08	0.00	0.00	0.43	0.00	0.00	**0.00**	0.03	0.11	0.00	0.10	0.38	0.21	0.47	0.00	0.00
PC	%medium sand	-0.332**	-0.345**	-0.17	-0.675**	-0.22	0.24	0.399**	-0.437**	0.13	-0.567**	-0.612**	**0.780****	-0.311**	0.20	-0.392**	0.313**	0.12	0.10	-0.03	-0.531**	-0.447**
S		0.01	0.00	0.17	0.00	0.07	0.05	0.00	0.00	0.29	0.00	0.00	**0.00**	0.01	0.09	0.00	0.01	0.35	0.41	0.83	0.00	0.00
PC	%fine sand	-0.485**	-0.414**	-0.21	**-0.714****	-0.13	0.314**	0.342**	-0.432**	0.23	-0.631**	**-0.767****	**0.781****	-0.351**	0.11	-0.22	0.22	0.271*	0.04	0.15	-0.692**	-0.573**
S		0.00	0.00	0.09	**0.00**	0.31	0.01	0.00	0.00	0.06	0.00	**0.00**	**0.00**	0.00	0.38	0.07	0.08	0.03	0.76	0.22	0.00	0.00
PC	%vfine sand	0.18	0.19	-0.08	0.06	-0.19	-0.262*	-0.08	-0.14	-0.09	-0.299*	-0.378**	0.05	0.285*	-0.16	0.06	0.04	0.03	-0.01	0.17	-0.375**	-0.401**
S		0.15	0.12	0.49	0.65	0.11	0.03	0.54	0.24	0.49	0.01	0.00	0.89	0.02	0.19	0.64	0.74	0.80	0.93	0.17	0.00	0.00
PC	%vcoarse silt	**0.837****	0.597**	0.357**	**0.847****	-0.21	-0.624**	-0.366**	0.19	-0.521**	0.284*	0.384**	**-0.779****	**0.787****	-0.420**	0.23	-0.255*	-0.22	-0.04	-0.285*	0.472**	0.18
S		**0.00**	0.00	0.00	**0.00**	0.08	0.00	0.00	0.13	0.00	0.02	0.00	**0.00**	**0.00**	0.00	0.06	0.04	0.07	0.72	0.02	0.00	0.14
PC	%coarse silt	0.534**	0.432**	0.265*	**0.784****	0.08	-0.354**	-0.365**	0.445**	-0.270*	0.606**	**0.728****	**-0.820****	.441**	-0.18	0.300*	-0.263*	-0.21	-0.08	-0.15	0.665**	0.486**
S		0.00	0.00	0.03	**0.00**	0.50	0.00	0.00	0.00	0.03	0.00	**0.00**	**0.00**	0.00	0.13	0.01	0.03	0.09	0.52	0.22	0.00	0.00
PC	%medium silt	-0.246*	-0.09	-0.09	0.09	0.393**	0.23	-0.10	0.333**	0.21	0.481**	0.551**	-0.258*	-0.305*	0.21	0.13	-0.11	-0.08	-0.04	0.13	0.377**	0.505**
S		0.04	0.48	0.48	0.49	0.00	0.06	0.40	0.01	0.09	0.00	0.00	0.03	0.01	0.09	0.31	0.37	0.52	0.73	0.29	0.00	0.00
PC	%fine silt	-0.415**	-0.19	-0.14	-0.09	0.450**	0.354**	-0.04	0.259*	0.305*	0.419**	0.452**	-0.11	-.0466**	0.257*	0.06	-0.06	-0.05	-0.03	0.17	0.297*	0.496**
S		0.00	0.11	0.27	0.46	0.00	0.00	0.72	0.03	0.01	0.00	0.00	0.36	0.00	0.03	0.53	0.64	0.70	0.82	0.17	0.01	0.00
PC	%vfine silt	-0.331**	-0.09	-0.04	0.06	0.501**	0.301*	-0.12	0.392**	0.289*	0.568**	0.583**	-0.268*	-0.406**	0.21	0.16	-0.07	-0.06	-0.03	0.13	0.440**	0.615**
S		0.01	0.45	0.73	0.61	0.00	0.01	0.34	0.00	0.02	0.00	0.00	0.03	0.00	0.08	0.19	0.59	0.61	0.78	0.28	0.00	0.00
PC	%clay	-0.16	0.05	0.08	0.284*	0.485**	0.18	-0.20	0.551**	0.22	**0.712****	**.709****	-0.459**	-0.254*	0.13	0.260*	-0.08	-0.07	-0.06	0.04	0.601**	0.688**
		0.19	0.67	0.49	0.02	0.00	0.13	0.10	0.00	0.07	**0.00**	**0.00**	0.00	0.04	0.30	0.03	0.53	0.54	0.65	0.72	0.00	0.00

Table 11: Upper Marsh Pearson Product Moment Correlations – Elements versus Grain Size

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
P C	PCB 18	-0.07	-0.05	0.01	-0.19	-0.11	0.04	0.04	-0.13	0.11	-0.15	-0.274*	0.16	-0.04	-0.07	-0.13	0.264*	-0.14	0.07	-0.03	0.04	-0.251*
S		0.55	0.70	0.92	0.13	0.37	0.74	0.72	0.31	0.36	0.23	0.02	0.21	0.75	0.59	0.28	0.03	0.25	0.58	0.82	0.72	0.04
P C	PCB 28	0.19	0.13	0.07	0.04	-0.15	-0.08	0.05	-0.02	-0.10	-0.08	-0.18	-0.06	0.14	-0.15	-0.10	0.20	-0.23	0.01	-0.13	0.11	-0.15
S		0.13	0.30	0.57	0.72	0.24	0.54	0.69	0.86	0.41	0.53	0.15	0.60	0.27	0.24	0.43	0.10	0.06	0.95	0.29	0.39	0.23
P C	PCB 52	0.03	0.00	0.00	-0.09	-0.19	-0.02	-0.01	-0.20	0.04	-0.24	-0.316**	0.14	0.00	-0.16	0.00	0.14	0.06	0.07	0.06	-0.08	-0.281*
S		0.82	0.97	1.00	0.46	0.12	0.86	0.96	0.10	0.74	0.05	0.01	0.24	0.99	0.19	0.99	0.26	0.61	0.59	0.62	0.51	0.02
PC	PCB 49	-0.02	-0.05	-0.02	-0.17	-0.16	0.07	0.09	-0.18	0.11	-0.24	-0.301*	0.20	-0.04	-0.18	-0.02	0.303*	-0.01	0.01	0.04	-0.14	-0.366**
S		0.89	0.71	0.87	0.18	0.19	0.55	0.46	0.15	0.39	0.05	0.01	0.10	0.73	0.15	0.86	0.01	0.92	0.92	0.74	0.25	0.00
PC	PCB 47	-0.06	-0.06	-0.04	-0.248*	-0.21	0.06	0.12	-0.264*	0.09	-0.268*	-0.365**	0.268*	-0.06	-0.12	-0.11	0.284*	-0.01	0.10	-0.04	-0.14	-0.380**
S		0.62	0.61	0.75	0.04	0.06	0.62	0.32	0.03	0.46	0.03	0.00	0.03	0.62	0.34	0.36	0.02	0.93	0.41	0.74	0.25	0.00
PC	PCB 44	0.01	0.04	-0.01	-0.10	-0.18	-0.03	0.01	-0.18	0.05	-0.21	-0.302*	0.14	0.00	-0.20	-0.03	0.16	-0.07	0.04	-0.01	-0.04	-0.300*
S		0.92	0.76	0.94	0.42	0.16	0.80	0.96	0.14	0.66	0.08	0.01	0.27	1.00	0.11	0.81	0.19	0.60	0.72	0.93	0.74	0.01
PC	PCB 66	-0.04	0.00	0.08	0.14	0.12	0.05	-0.05	0.346**	0.17	0.22	0.17	-0.15	-0.04	0.04	0.07	-0.05	0.03	0.16	-0.02	0.292*	0.268*
S		0.75	0.97	0.53	0.26	0.35	0.69	0.70	0.00	0.17	0.08	0.16	0.24	0.75	0.72	0.55	0.72	0.60	0.19	0.89	0.02	0.03
PC	PCB 101	0.05	-0.04	-0.02	-0.09	-0.22	-0.10	0.06	-0.19	0.03	-0.262*	-0.290*	0.10	0.01	-0.17	-0.02	0.01	-0.01	-0.04	-0.04	0.03	-0.295*
S		0.70	0.73	0.90	0.46	0.07	0.42	0.65	0.12	0.81	0.03	0.02	0.44	0.93	0.17	0.88	0.91	0.92	0.75	0.73	0.79	0.02
PC	PCB 151	0.01	-0.05	0.07	-0.15	-0.15	-0.05	-0.07	-0.294*	0.04	-0.314**	-0.389**	0.10	0.09	-0.17	-0.16	0.18	-0.07	0.11	-0.09	0.01	-0.346**
S		0.94	0.89	0.55	0.24	0.23	0.67	0.59	0.02	0.73	0.01	0.00	0.41	0.46	0.16	0.20	0.15	0.60	0.39	0.46	0.93	0.00
PC	PCB 118	0.07	0.03	-0.03	-0.06	-0.21	-0.03	0.07	-0.20	-0.02	-0.16	-0.254*	0.11	-0.03	-0.14	0.04	0.10	-0.01	-0.01	-0.02	0.04	-0.279*
S		0.55	0.81	0.83	0.61	0.09	0.83	0.55	0.10	0.85	0.21	0.04	0.40	0.84	0.25	0.75	0.42	0.94	0.92	0.87	0.77	0.02
PC	PCB 153	0.01	-0.03	0.05	-0.09	-0.20	0.00	-0.02	-0.250*	0.02	-0.24	-0.348**	0.11	0.05	-0.19	0.00	0.08	-0.06	0.04	-0.05	0.01	-0.272*
S		0.94	0.79	0.69	0.47	0.10	0.98	0.85	0.04	0.88	0.05	0.00	0.36	0.70	0.12	0.99	0.50	0.66	0.76	0.69	0.95	0.03
PC	PCB 105	-0.06	-0.05	0.07	-0.13	-0.09	0.06	-0.03	-0.21	0.12	-0.19	-0.286*	0.16	-0.03	-0.18	0.02	0.12	-0.06	0.07	0.05	-0.05	-0.350**
S		0.64	0.71	0.57	0.31	0.47	0.60	0.80	0.09	0.32	0.13	0.02	0.20	0.79	0.14	0.85	0.35	0.62	0.56	0.66	0.89	0.00
P C	PCB 141	0.02	-0.05	0.05	-0.19	-0.22	0.00	0.18	-0.20	-0.02	-0.22	-0.312*	0.19	0.05	-0.19	-0.18	0.246*	0.00	0.04	-0.282*	-0.04	-0.307*
S		0.85	0.89	0.68	0.13	0.07	0.98	0.14	0.11	0.86	0.07	0.01	0.12	0.71	0.12	0.16	0.04	0.97	0.72	0.02	0.74	0.01
PC	PCB 138	0.02	-0.03	-0.05	-0.16	-0.241*	-0.03	0.07	-0.276*	-0.06	-0.260*	-0.371**	0.15	0.01	-0.12	-0.13	0.20	-0.12	0.03	-0.11	-0.05	-0.296*
S		0.86	0.82	0.71	0.20	0.05	0.79	0.58	0.02	0.65	0.02	0.00	0.24	0.91	0.32	0.29	0.11	0.35	0.81	0.37	0.66	0.02
P C	PCB 183	-0.06	-0.01	-0.08	-0.15	-0.20	-0.01	0.00	-0.21	0.11	-0.23	-0.342**	0.18	-0.06	-0.14	0.00	0.20	-0.05	0.03	0.03	-0.04	-0.287*
S		0.64	0.95	0.54	0.22	0.11	0.96	0.98	0.08	0.38	0.06	0.00	0.14	0.63	0.26	0.97	0.11	0.72	0.81	0.78	0.73	0.02
PC	PCB 128	0.05	0.02	0.02	-0.06	-0.14	-0.03	0.01	-0.242*	0.01	-0.24	-0.353**	0.13	-0.01	-0.15	0.07	0.08	0.07	0.10	0.07	-0.15	-0.331**
S		0.89	0.89	0.89	0.64	0.24	0.80	0.93	0.05	0.91	0.05	0.00	0.28	0.92	0.22	0.56	0.54	0.60	0.41	0.56	0.21	0.01
PC	PCB 156	-0.01	0.03	-0.09	-0.21	-0.299*	-0.03	0.272*	-0.24	0.03	-0.20	-0.311*	0.22	-0.06	-0.19	-0.03	0.19	0.07	0.08	-0.01	-0.13	-0.304*
S		0.92	0.84	0.46	0.08	0.01	0.84	0.03	0.05	0.80	0.11	0.01	0.07	0.84	0.12	0.81	0.13	0.55	0.52	0.97	0.30	0.01
P C	PCB 180	-0.01	-0.01	0.03	-0.06	-0.08	-0.13	-0.12	-0.18	0.04	-0.20	-0.296*	0.06	0.00	-0.06	-0.05	0.05	0.02	0.09	0.04	0.00	-0.251*
S		0.93	0.94	0.83	0.63	0.50	0.30	0.32	0.15	0.75	0.10	0.01	0.63	1.00	0.62	0.70	0.67	0.86	0.48	0.73	0.99	0.04
PC	PCB 170	-0.15	-0.07	0.04	-0.19	-0.08	0.03	0.02	-0.283*	0.17	-0.277*	-0.398**	0.23	-0.06	-0.06	-0.04	-0.03	0.06	0.264*	0.05	-0.21	-0.358**
S		0.23	0.58	0.75	0.13	0.51	0.79	0.87	0.02	0.16	0.02	0.00	0.07	0.62	0.63	0.73	0.82	0.66	0.03	0.67	0.09	0.00
PC	PCB 194	-0.06	-0.20	-0.07	-0.21	-0.243*	0.06	0.10	-0.329**	-0.01	-0.372**	-0.429**	0.336**	-0.05	0.03	0.00	0.09	0.09	0.03	0.01	-0.338**	-0.334**
S		0.64	0.10	0.56	0.09	0.05	0.66	0.42	0.01	0.91	0.00	0.00	0.01	0.67	0.80	1.00	0.47	0.45	0.79	0.96	0.01	0.01
PC	TOTAL PCB	0.01	-0.01	0.00	-0.13	-0.20	-0.02	0.05	-0.21	0.05	-0.24	-0.347**	0.15	0.00	-0.16	-0.05	0.18	-0.03	0.08	-0.02	-0.04	-0.316**
S		0.96	0.93	0.98	0.29	0.11	0.88	0.69	0.09	0.67	0.05	0.00	0.22	0.98	0.20	0.70	0.15	0.79	0.54	0.85	0.75	0.01

Table 12: Upper Marsh Pearson Product Moment Correlations – Elements versus PCBs

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
PC	Ace	0.10	0.09	0.00	0.15	0.08	-0.09	-0.15	0.19	0.00	0.20	0.21	-0.23	0.15	0.16	-0.04	.252*	-0.16	-0.08	-0.06	0.20	0.00
S		0.44	0.45	0.97	0.23	0.51	0.48	0.22	0.12	0.97	0.10	0.08	0.06	0.24	0.20	0.74	0.04	0.19	0.54	0.61	0.10	0.98
PC	Flu	0.08	0.05	0.18	0.20	0.18	-0.04	-0.17	0.323**	0.05	0.340**	0.352**	-0.313**	0.16	0.18	0.03	0.21	-0.19	-0.12	-0.10	0.329**	0.08
S		0.50	0.71	0.15	0.10	0.13	0.74	0.18	0.01	0.70	0.00	0.00	0.01	0.19	0.14	0.81	0.09	0.12	0.32	0.41	0.01	0.53
PC	Phe	0.08	0.17	0.10	0.254*	0.10	-0.06	-0.08	0.357**	0.07	0.344**	0.291*	-0.23	0.09	0.08	0.19	0.09	-0.02	0.10	0.03	0.16	0.280*
S		0.51	0.18	0.41	0.04	0.40	0.60	0.51	0.00	0.60	0.00	0.02	0.06	0.48	0.51	0.12	0.45	0.85	0.40	0.78	0.19	0.02
PC	Anth	0.01	0.05	-0.06	0.09	0.11	0.00	-0.09	0.21	0.13	0.00	-0.01	-0.07	-0.02	-0.01	0.06	0.05	0.05	0.04	0.11	0.05	0.07
S		0.91	0.70	0.65	0.45	0.37	0.99	0.46	0.08	0.30	1.00	0.93	0.56	0.89	0.94	0.66	0.68	0.70	0.76	0.39	0.66	0.59
PC	Fluranth	0.23	0.261*	-0.04	0.23	-0.01	-0.19	-0.11	0.09	-0.07	0.11	0.19	-0.275*	0.273*	0.13	-0.15	0.03	-0.16	-0.01	-0.17	0.13	0.18
S		0.06	0.03	0.77	0.06	0.94	0.12	0.36	0.47	0.55	0.37	0.13	0.02	0.02	0.29	0.23	0.78	0.21	0.95	0.16	0.29	0.14
PC	Pyr	0.16	0.23	0.08	0.11	0.06	-0.14	-0.11	0.01	-0.09	0.00	0.08	-0.20	0.276*	0.09	-0.22	0.05	-0.17	-0.03	-0.245*	0.08	0.09
S		0.19	0.05	0.49	0.36	0.62	0.25	0.36	0.92	0.48	0.98	0.52	0.11	0.02	0.47	0.08	0.69	0.15	0.84	0.04	0.49	0.47
PC	Chrys	0.12	-0.01	0.14	0.15	0.11	-0.06	-0.09	0.10	-0.13	0.18	0.276*	-0.280*	0.14	-0.03	0.00	-0.12	-0.22	-0.14	-0.14	0.255*	0.14
S		0.33	0.94	0.26	0.22	0.36	0.65	0.44	0.44	0.28	0.15	0.02	0.02	0.24	0.82	1.00	0.32	0.07	0.25	0.24	0.04	0.26
PC	Benzanth	0.07	0.13	0.02	0.02	0.05	-0.11	-0.11	-0.02	-0.09	-0.11	0.00	-0.12	0.260*	0.16	-0.19	0.03	-0.19	-0.06	-0.18	-0.05	0.00
S		0.58	0.30	0.86	0.86	0.71	0.39	0.39	0.87	0.47	0.36	1.00	0.31	0.03	0.21	0.13	0.78	0.12	0.60	0.15	0.71	0.97
PC	Benzbfluranth	0.00	0.00	-0.04	-0.05	0.07	-0.03	-0.05	-0.02	-0.04	-0.16	-0.03	-0.06	0.14	0.09	-0.14	-0.07	-0.21	-0.15	-0.06	-0.03	-0.04
S		1.00	0.99	0.76	0.67	0.57	0.63	0.67	0.87	0.76	0.19	0.84	0.60	0.26	0.45	0.25	0.55	0.08	0.23	0.61	0.82	0.74
PC	Benzkfluranth	0.02	0.05	-0.10	0.01	-0.02	-0.08	-0.03	0.01	-0.06	0.00	0.04	-0.10	0.244*	0.18	-0.03	0.07	-0.24	-0.20	0.02	-0.16	-0.05
S		0.85	0.69	0.41	0.93	0.85	0.53	0.79	0.94	0.61	0.97	0.76	0.42	0.05	0.15	0.80	0.59	0.05	0.09	0.88	0.20	0.71
PC	Benzopyr	0.03	0.01	-0.09	0.00	-0.03	-0.09	-0.03	-0.01	-0.08	-0.03	-0.02	-0.08	0.244*	0.19	-0.05	0.03	-0.20	-0.19	0.05	-0.18	-0.10
S		0.83	0.91	0.44	0.99	0.80	0.47	0.80	0.93	0.51	0.79	0.90	0.52	0.04	0.13	0.71	0.81	0.10	0.11	0.68	0.15	0.40
PC	Indeno123cdpyr	-0.04	-0.04	-0.17	-0.09	-0.05	-0.03	0.01	-0.10	-0.06	-0.16	-0.10	0.02	0.13	0.23	-0.06	-0.04	-0.16	-0.22	0.09	-0.24	-0.11
S		0.77	0.75	0.15	0.46	0.70	0.78	0.94	0.44	0.60	0.20	0.43	0.86	0.28	0.06	0.62	0.78	0.20	0.07	0.48	0.05	0.38
PC	benzghiperyl	-0.02	-0.02	-0.18	-0.09	-0.04	-0.02	0.00	-0.13	-0.08	-0.21	-0.12	0.03	0.13	0.17	-0.06	-0.06	-0.14	-0.23	0.08	-0.239*	-0.10
S		0.87	0.85	0.14	0.47	0.77	0.88	0.97	0.30	0.54	0.08	0.33	0.80	0.31	0.17	0.64	0.65	0.24	0.05	0.53	0.05	0.43
PC	dibenzahanth	-0.01	0.01	-0.13	-0.02	-0.01	-0.09	-0.02	-0.01	-0.04	-0.06	-0.04	-0.05	0.15	0.20	-0.01	0.00	-0.11	-0.20	0.16	-0.24	-0.08
S		0.93	0.96	0.28	0.86	0.92	0.46	0.85	0.90	0.72	0.63	0.77	0.71	0.22	0.11	0.94	0.99	0.35	0.10	0.18	0.05	0.50
PC	totalpah	0.06	0.05	-0.04	0.03	0.04	-0.08	-0.07	0.01	-0.09	-0.05	0.05	-0.15	0.23	0.15	-0.10	-0.03	-0.239*	-0.18	-0.06	-0.04	0.00
S		0.63	0.67	0.74	0.81	0.74	0.50	0.56	0.94	0.48	0.68	0.67	0.24	0.06	0.23	0.40	0.81	0.05	0.14	0.62	0.75	0.99
PC	TOC	-0.363**	-0.18	-0.359**	-0.303*	-0.02	0.14	0.261*	0.10	0.248*	0.20	0.10	0.348**	-0.455**	0.306*	0.02	0.22	0.10	-0.12	0.272*	-0.331**	0.19
S		0.00	0.14	0.00	0.01	0.90	0.26	0.03	0.43	0.04	0.10	0.41	0.00	0.00	0.01	0.86	0.07	0.42	0.33	0.03	0.01	0.12

Table 13: Upper Marsh Pearson Product Moment Correlations – Elements versus PAHs

		PCB18	PCB28	PCB52	PCB49	PCB47	PCB44	PCB66	PCB101	PCB151	PCB118	PCB153	PCB105	PCB141	PCB138	PCB183	PCB128	PCB156	PCB180	PCB170	PCB194	TOTALPCB
P C	1 8	1.00	0.771**	0.859**	0.731**	0.822**	0.865**	0.309*	0.564**	0.829**	0.757**	0.885**	0.803**	0.688**	0.803**	0.803**	0.788**	0.714**	0.788**	0.644**	0.454**	0.906**
S			0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P C	2 8	0.771**	1.00	0.621**	0.551**	0.650**	0.734**	0.401**	0.510**	0.651**	0.690**	0.700**	0.468**	0.681**	0.792**	0.680**	0.670**	0.563**	0.674**	0.431**	0.511**	0.790**
S		0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P C	5 2	0.859**	0.621**	1.00	0.825**	0.886**	0.902**	0.16	0.593**	0.814**	0.829**	0.865**	0.778**	0.641**	0.808**	0.820**	0.871**	0.780**	0.788**	0.685**	0.522**	0.910**
S		0.00	0.00		0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	4 9	0.731**	0.551**	0.825**	1.00	0.872**	0.834**	0.14	0.514**	0.708**	0.685**	0.683**	0.697**	0.636**	0.725**	0.734**	0.725**	0.682**	0.550**	0.580**	0.537**	0.805**
S		0.00	0.00	0.00		0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	4 7	0.822**	0.650**	0.886**	0.872**	1.00	0.934**	0.16	0.641**	0.834**	0.842**	0.819**	0.731**	0.747**	0.887**	0.885**	0.843**	0.813**	0.719**	0.702**	0.622**	0.927**
S		0.00	0.00	0.00	0.00		0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	4 4	0.865**	0.734**	0.902**	0.834**	0.934**	1.00	0.255*	0.657**	0.867**	0.840**	0.890**	0.772**	0.728**	0.900**	0.909**	0.861**	0.772**	0.805**	0.706**	0.579**	0.955**
S		0.00	0.00	0.00	0.00	0.00		0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	6 6	0.309*	0.401**	0.16	0.14	0.16	0.255*	1.00	0.302*	0.22	0.16	0.253*	0.15	0.22	0.22	0.19	0.09	0.07	0.270*	0.15	0.09	0.301*
S		0.01	0.00	0.19	0.27	0.20	0.04		0.01	0.07	0.20	0.04	0.22	0.07	0.07	0.13	0.45	0.57	0.03	0.21	0.49	0.01
PC	1 0 1	0.564**	0.510**	0.593**	0.514**	0	0.657**	0.302*	1.00	0.676**	0.694**	0.646**	0.553**	0.487**	0.649**	0.691**	0.587**	0.652**	0.656**	0.576**	0.535**	0.734**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.01		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	1 5 1	0.829**	0.651**	0.814**	0.708**	0.834**	0.867**	0.22	0.676**	1.00	0.805**	0.908**	0.805**	0.708**	0.851**	0.869**	0.815**	0.663**	0.828**	0.775**	0.539**	0.908**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	1 1 8	0.757**	0.690**	0.829**	0.685**	0.842**	0.840**	0.16	0.694**	0.805**	1.00	0.845**	0.688**	0.690**	0.895**	0.886**	0.838**	0.757**	0.814**	0.677**	0.604**	0.902**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	1 5 3	0.885**	0.700**	0.865**	0.683**	0.819**	0.890**	0.253*	0.646**	0.908**	0.845**	1.00	0.858**	0.702**	0.871**	0.890**	0.849**	0.705**	0.852**	0.796**	0.590**	0.936**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	1 0 5	0.803**	0.468**	0.778**	0.697**	0.731**	0.772**	0.15	0.553**	00.805**	0.688**	0.858**	1.00	0.558**	0.648**	0.778**	0.758**	0.628**	0.695**	0.802**	0.485**	0.809**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	1 4 1	0.688**	0.681**	0.641**	0.636**	0.747**	0.728**	0.22	0.487**	0.708**	0.690**	0.702**	0.558**	1.00	0.816**	0.731**	0.659**	0.653**	0.581**	0.531**	0.506**	0.775**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P C	1 3 8	0.803**	0.792**	0.808**	0.725**	.887**	0.900**	0.22	0.649**	0.851**	0.895**	0.871**	0.648**	0.816**	1.00	0.908**	0.806**	0.720**	0.802**	0.680**	0.657**	0.929**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	1 8 3	0.803**	0.680**	0.820**	0.734**	.885**	0.909**	0.19	0.691**	0.869**	0.886**	0.890**	0.778**	0.731**	0.908**	1.00	0.839**	0.798**	0.799**	0.772**	0.634**	0.939**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00
P C	1 2 8	0.788**	0.670**	0.871**	0.725**	.843**	0.861**	0.09	0.587**	0.815**	0.835**	0.849**	0.758**	0.659**	0.806**	0.839**	1.00	0.808**	0.789**	0.749**	0.651**	0.906**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PC	1 5 6	0.714**	0.563**	0.780**	0.682**	0.813**	0.772**	0.07	0.652**	0.663**	0.757**	0.705**	0.628**	0.653**	0.720**	0.798**	0.808**	1.00	0.626**	0.613**	0.514**	0.829**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
PC	1 8 0	0.788**	0.674**	0.788**	0.550**	0.719**	0.805**	0.270*	0.656**	0.828**	0.814**	0.852**	0.695**	0.581**	0.802**	0.799**	0.789**	0.626**	1.00	0.739**	0.512**	0.863**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00
P C	1 7 0	0.644**	0.431**	0.685**	0.580**	0.702**	0.706**	0.15	0.576**	0.775**	0.677**	0.796**	0.802**	0.531**	0.680**	0.772**	0.749**	0.613**	0.739**	1.00	0.574**	0.775**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00
PC	1 9 4	0.454**	0.511**	0.522**	0.537**	0.622**	0.579**	0.09	0.535**	0.539**	0.604**	0.590**	0.485**	0.506**	0.657**	0.634**	0.651**	0.514**	0.512**	0.574**	1.00	0.654**
S		0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
PC	total	0.906**	0.790**	.910**	0.805**	0.927**	0.955**	0.301*	0.734**	0.908**	0.902**	.936**	0.809**	0.775**	0.929**	0.939**	0.906**	0.829**	0.863**	0.775**	0.654**	1.00
S		0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

Table 14: Upper Marsh Pearson Product Moment Correlations – PCBs versus PCBs

		PCB 18	PCB 28	PCB 52	PCB 49	PCB 47	PCB 44	PCB 66	PCB 101	PCB 151	PCB 118	PCB 153	PCB 105	PCB 141	PCB 138	PCB 183	PCB 128	PCB 156	PCB 180	PCB 170	PC B194	TOTAL PCB
P C	χ L F	-0.20	0.03	-0.21	-0.21	-0.257*	-0.19	0.17	-0.18	-0.283*	-0.11	-0.19	-0.23	-0.11	-0.20	-0.24	-0.22	-0.17	-0.23	-0.369**	-0.278*	-0.21
S		0.11	0.79	0.09	0.10	0.04	0.13	0.18	0.14	0.02	0.37	0.12	0.06	0.36	0.11	0.05	0.07	0.18	0.06	0.00	0.02	0.09
P	F D %	-0.01	-0.04	-0.04	-0.08	-0.07	-0.09	-0.14	-0.03	-0.14	0.01	-0.03	-0.01	-0.03	-0.06	-0.08	0.05	0.10	-0.05	0.04	-0.05	-0.04
S		0.94	0.75	0.77	0.54	0.59	0.47	0.25	0.79	0.26	0.91	0.84	0.91	0.82	0.62	0.54	0.70	0.41	0.70	0.74	0.71	0.73
PC	S I R M	-0.19	0.04	-0.22	-0.17	-0.243*	-0.18	0.22	-0.18	-0.299*	-0.14	-0.22	-0.263*	-0.13	-0.20	-0.247*	-0.264*	-0.19	-0.251*	-0.414**	-0.282*	-0.22
S		0.11	0.77	0.07	0.16	0.05	0.14	0.08	0.14	0.01	0.26	0.08	0.03	0.31	0.11	0.04	0.03	0.11	0.04	0.00	0.02	0.08
PC	χ A R M	-0.246*	-0.05	-0.352**	-0.262*	-0.315**	-0.328**	0.15	-0.270*	-0.467**	-0.22	-0.370**	-0.372**	-0.14	-0.24	-0.330**	-0.419**	-0.22	-0.403**	-0.525**	-0.23	-.0326**
S		0.04	0.68	0.00	0.03	0.01	0.01	0.23	0.03	0.00	0.07	0.00	0.00	0.27	0.05	0.01	0.00	0.07	0.00	0.00	0.06	0.01
PC	χARM/SIRM	-0.12	-0.07	-0.22	-0.13	-0.13	-0.23	-0.04	-0.15	-0.299*	-0.12	-0.257*	-0.22	-0.02	-0.08	-0.17	-0.272*	-0.07	-0.280*	-0.273*	0.03	-0.19
S		0.35	0.56	0.07	0.28	0.30	0.06	0.73	0.23	0.01	0.35	0.04	0.07	0.87	0.54	0.17	0.03	0.59	0.02	0.03	0.83	0.13
PC	SIRM/χLF	-0.01	0.04	-0.09	0.14	0.04	0.00	0.267*	-0.03	-0.11	-0.13	-0.15	-0.20	-0.08	-0.02	-0.07	-0.245*	-0.17	-0.14	-0.309*	-0.06	-0.07
S		0.91	0.74	0.46	0.27	0.74	0.97	0.03	0.83	0.38	0.30	0.23	0.11	0.51	0.88	0.57	0.05	0.18	0.25	0.01	0.60	0.57
PC	χARM/χLF	-0.11	-0.06	-0.23	-0.11	-0.12	-0.22	0.01	-0.15	-0.307*	-0.14	-0.274*	-0.250*	-0.03	-0.08	-0.18	-0.306*	-0.10	-0.295*	-0.318**	0.01	-0.19
S		0.36	0.61	0.06	0.37	0.33	0.07	0.96	0.24	0.01	0.27	0.02	0.04	0.78	0.53	0.15	0.01	0.44	0.02	0.01	0.91	0.11
PC	H I R M	-0.21	-0.14	-0.23	-0.23	-0.291*	-0.21	0.20	-0.22	-0.22	-0.22	-0.241*	-0.266*	-0.15	-0.249*	-0.259*	-0.286*	-0.285*	-0.14	-0.306*	-0.383**	-0.254*
S		0.08	0.25	0.06	0.06	0.02	0.08	0.10	0.08	0.08	0.07	0.05	0.03	0.23	0.04	0.03	0.02	0.02	0.28	0.01	0.00	0.04
PC	H A R D %	0.08	-0.16	0.12	0.05	0.10	0.08	-0.15	0.08	0.22	0.02	0.10	0.15	0.05	0.06	0.13	0.15	0.05	0.249*	0.335**	0.07	0.09
S		0.50	0.19	0.33	0.67	0.43	0.50	0.22	0.52	0.07	0.86	0.42	0.22	0.68	0.61	0.28	0.22	0.66	0.04	0.01	0.56	0.45
PC	A R M	-0.246*	-0.05	-0.352**	-0.262*	-0.315**	-0.328**	0.15	-0.270*	-0.467**	-0.22	-0.370**	-0.372**	-0.14	-0.24	-0.330**	-0.419**	-0.22	-0.403**	-0.525**	-0.23	-0.326**
S		0.04	0.68	0.00	0.03	0.01	0.01	0.23	0.03	0.00	0.07	0.00	0.00	0.27	0.05	0.01	0.00	0.07	0.00	0.00	0.06	0.01
PC	SIRM/ARM	0.14	0.08	0.247*	0.18	0.17	0.261*	0.03	0.18	0.344**	0.12	.285*	0.243*	0.07	0.11	0.19	0.295*	0.09	0.301*	0.302*	0.03	0.22
S		0.25	0.50	0.04	0.16	0.16	0.03	0.81	0.15	0.00	0.33	0.02	0.05	0.60	0.38	0.13	0.02	0.47	0.01	0.01	0.82	0.08
P C	S o f t	-0.22	0.04	-0.22	-0.14	-0.23	-0.18	0.23	-0.13	-0.283*	-0.15	-0.24	-0.279*	-0.16	-0.20	-0.243*	-0.270*	-0.21	-0.247*	-0.404**	-0.283*	-0.21
S		0.08	0.74	0.07	0.25	0.06	0.15	0.06	0.28	0.03	0.24	0.05	0.02	0.21	0.11	0.05	0.03	0.10	0.04	0.00	0.02	0.09
PC	- 2 0 m T	-0.14	0.06	-0.09	0.02	-0.07	-0.07	0.16	0.07	-0.02	-0.07	-0.17	-0.18	-0.12	-0.07	-0.09	-0.14	-0.11	-0.10	-0.19	-0.14	-0.08
S		0.27	0.65	0.46	0.84	0.55	0.58	0.19	0.57	0.89	0.57	0.17	0.14	0.32	0.55	0.46	0.27	0.37	0.43	0.12	0.25	0.54
P C	- 3 0 0 m T	-0.08	0.16	-0.12	-0.05	-0.10	-0.08	0.15	-0.08	-0.22	-0.02	-0.10	-0.15	-0.05	-0.06	-0.13	-0.15	-0.05	-0.249*	-0.335**	-0.07	-0.09
S		0.50	0.19	0.33	0.67	0.43	0.50	0.22	0.52	0.07	0.86	0.42	0.22	0.68	0.61	0.28	0.22	0.66	0.04	0.01	0.56	0.45

Table 15: Upper Marsh Pearson Product Moment Correlations – PCBs versus Magnetics

		PCB 18	PCB 28	PCB 52	PCB 49	PCB 47	PCB 44	PCB 66	PCB 101	PCB 151	PCB 118	PCB 153	PCB 105	PCB 141	PCB 138	PCB 183	PCB 128	PCB 156	PCB 180	PCB 170	PC B194	TOTAL PCB
P C	Mean	0.303*	0.22	0.324**	0.382**	0.466**	0.341**	-0.18	0.314**	0.314**	0.282*	0.314**	0.272*	0.441**	0.381**	0.334**	0.367**	0.409**	0.23	0.376**	0.473**	0.371**
S		0.01	0.07	0.01	0.00	0.00	0.00	0.14	0.01	0.01	0.02	0.01	0.03	0.00	0.00	0.01	0.00	0.00	0.06	0.00	0.00	0.00
P C	Sorting	0.246*	0.06	0.24	0.319**	0.381**	0.23	-0.15	0.19	0.20	0.18	0.21	0.23	0.311*	0.269*	0.259*	0.23	0.284*	0.14	0.340**	0.360**	0.255*
S		0.04	0.66	0.05	0.01	0.00	0.06	0.22	0.12	0.10	0.16	0.09	0.06	0.01	0.03	0.03	0.06	0.02	0.26	0.00	0.00	0.04
P C	Skewness	0.15	-0.11	0.13	0.23	0.245*	0.10	-0.18	0.08	0.10	0.06	0.08	0.16	0.13	0.13	0.16	0.08	0.16	0.03	.247*	0.24	0.12
S		0.24	0.38	0.30	0.06	0.05	0.41	0.15	0.51	0.42	0.62	0.55	0.20	0.29	0.29	0.20	0.53	0.21	0.80	0.04	0.05	0.35
PC	Kurtosis	-0.12	0.06	-0.08	-0.15	-0.16	-0.12	0.15	-0.12	-0.08	0.02	0.02	-0.10	-0.04	-0.06	-0.12	-0.10	-0.24	-0.12	-0.245*	0.03	-0.10
S		0.32	0.65	0.54	0.23	0.18	0.32	0.24	0.35	0.51	0.89	0.90	0.44	0.74	0.63	0.35	0.42	0.05	0.34	0.05	0.81	0.43
PC	%Sand	0.291*	0.13	0.309*	0.377**	0.433**	0.310*	-0.19	0.266*	0.289*	0.24	0.283*	0.288*	0.372**	0.331**	0.321**	0.338**	0.368**	0.22	0.407**	0.422**	0.335**
S		0.02	0.30	0.01	0.00	0.00	0.01	0.12	0.03	0.02	0.05	0.02	0.02	0.00	0.01	0.01	0.01	0.00	0.07	0.00	0.00	0.01
PC	%Mud	0-.291*	-0.13	-0.309*	-0.377**	-0.433**	-0.310*	0.19	-0.266*	-0.289*	-0.24	-0.283*	-0.288*	-0.372**	-0.331**	-0.321**	-0.338**	-0.368**	-0.22	-0.407**	-0.422**	-0.335**
S		0.02	0.30	0.01	0.00	0.00	0.01	0.12	0.03	0.02	0.05	0.02	0.02	0.00	0.01	0.01	0.01	0.00	0.07	0.00	0.00	0.01
PC	%vcoarse sand	0.04	-0.02	0.02	0.03	0.14	0.04	-0.04	0.00	-0.02	0.00	-0.03	-0.02	0.07	0.05	-0.02	-0.06	-0.04	-0.03	0.01	0.23	0.01
S		0.76	0.88	0.89	0.82	0.26	0.75	0.73	0.98	0.90	0.99	0.83	0.84	0.55	0.71	0.88	0.64	0.72	0.81	0.96	0.07	0.95
PC	%coarse sand	0.16	0.08	0.13	0.21	0.323**	0.16	-0.11	0.17	0.12	0.13	0.12	0.10	0.256*	0.22	0.17	0.10	0.19	0.02	0.17	0.363**	0.17
S		0.18	0.53	0.30	0.09	0.01	0.19	0.38	0.17	0.35	0.30	0.35	0.44	0.04	0.08	0.17	0.44	0.12	0.90	0.18	0.00	0.17
PC	%medium sand	0.21	0.12	0.18	0.298*	0.378**	0.21	-0.14	0.22	0.19	0.18	0.18	0.16	0.338**	0.293*	0.263*	0.19	0.296*	0.08	0.262*	0.361**	0.246*
S		0.08	0.33	0.15	0.01	0.00	0.08	0.26	0.08	0.12	0.13	0.15	0.20	0.01	0.02	0.03	0.12	0.02	0.53	0.03	0.00	0.04
PC	%fine sand	0.283*	0.07	0.313**	0.356**	0.381**	0.273*	-0.18	0.21	0.268*	0.21	0.276*	0.302*	0.343**	0.285*	0.279*	0.325**	0.320**	0.23	0.412**	0.354**	0.302*
S		0.02	0.59	0.01	0.00	0.00	0.03	0.15	0.09	0.03	0.09	0.02	0.01	0.00	0.02	0.02	0.01	0.01	0.06	0.00	0.00	0.01
PC	%vfine sand	0.20	0.20	0.284*	0.256*	0.265*	0.328**	-0.16	0.265*	0.296*	0.23	0.267*	0.261*	0.18	0.23	0.281*	0.395**	0.332**	0.328**	0.331**	0.289*	0.308*
S		0.10	0.10	0.02	0.04	0.03	0.01	0.20	0.02	0.01	0.06	0.03	0.03	0.15	0.06	0.02	0.00	0.01	0.01	0.01	0.02	0.01
PC	%vcoarse silt	-0.08	0.19	-0.04	-0.13	-0.13	0.00	0.11	0.03	0.01	0.04	0.04	-0.06	-0.01	-0.02	-0.06	0.03	-0.05	0.04	-0.14	-0.06	0.00
S		0.51	0.12	0.77	0.29	0.31	0.99	0.37	0.79	0.94	0.77	0.75	0.60	0.93	0.89	0.64	0.79	0.68	0.74	0.25	0.62	0.97
P C	%coarsesilt	-0.252*	-0.04	-0.252*	-0.336**	-0.373**	-0.260*	0.18	-0.22	-0.248*	-0.18	-0.23	-0.271*	-0.290*	-0.271*	-0.292*	-0.266*	-0.310*	-0.19	-0.394**	-0.338**	-0.275*
S		0.04	0.74	0.04	0.01	0.00	0.03	0.14	0.08	0.04	0.15	0.07	0.03	0.02	0.03	0.02	0.03	0.01	0.12	0.00	0.01	0.02
PC	%medium silt	-0.305*	-0.337**	-0.357**	-0.347**	-0.425**	-0.387**	0.09	-0.333**	-0.357**	-0.329**	-0.397**	-0.302*	-0.461**	-0.392**	-0.343**	-0.458**	-0.399**	-0.327**	-0.384**	-0.440**	-0.415**
S		0.01	0.01	0.00	0.00	0.00	0.00	0.49	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
P C	%fine silt	-0.255*	-0.354**	-0.321**	-0.295*	-0.368**	-0.343**	0.08	-0.313**	-0.313**	-0.310*	-0.356**	-0.24	-0.427**	-.0355**	-0.286*	-0.421**	-0.360**	-0.281*	-0.294*	-0.423**	-0.372**
S		0.04	0.00	0.01	0.02	0.00	0.00	0.51	0.01	0.01	0.01	0.00	0.05	0.00	0.00	0.02	0.00	0.00	0.02	0.02	0.00	0.00
PC	%vfine silt	-0.249*	-0.314**	-0.318**	-0.318**	-0.391**	-0.339**	0.18	-0.346**	-0.329**	-0.312*	-0.342**	-0.252*	-0.424**	-0.365**	-0.304*	-0.404**	-0.386**	-0.283*	-0.314**	-0.474**	-0.371**
S		0.04	0.01	0.01	0.01	0.00	0.01	0.15	0.00	0.01	0.01	0.00	0.04	0.00	0.00	0.01	0.00	0.00	0.03	0.01	0.00	0.00
PC	%clay	-0.24	-0.23	-0.306*	-0.347**	-0.405**	-0.327**	0.264*	-0.365**	-0.336**	-0.288*	-0.299*	-0.261*	-0.368**	-0.352**	-0.313**	-0.356**	-0.396**	-0.23	-0.325**	-0.479**	-0.350**
		0.05	0.06	0.01	0.00	0.00	0.01	0.03	0.00	0.01	0.02	0.01	0.03	0.00	0.00	0.01	0.00	0.00	0.07	0.01	0.00	0.00

Table 16: Upper Marsh Pearson Product Moment Correlations – PCBs versus Grain Size

		PCB 18	PCB 28	PCB 52	PCB 49	PCB 47	PCB 44	PCB 66	PCB 101	PCB 151	PCB 118	PCB 153	PCB 105	PCB 141	PCB 138	PCB 183	PCB 128	PCB 156	PCB 180	PCB 170	PC B194	TOTAL PCB
P C	A c e	0.250*	0.290*	0.19	0.07	0.15	0.19	0.04	0.02	0.18	0.20	0.12	-0.04	0.14	0.24	0.13	0.10	0.05	0.22	-0.14	-0.09	0.16
S		0.04	0.02	0.12	0.59	0.24	0.12	0.72	0.85	0.14	0.11	0.32	0.72	0.27	0.05	0.30	0.43	0.69	0.07	0.26	0.48	0.20
P C	F l u	0.16	0.14	0.05	0.00	-0.04	-0.01	0.14	-0.12	-0.01	-0.03	0.01	-0.06	-0.01	0.00	-0.08	-0.08	-0.16	0.09	-0.21	-0.22	-0.01
S		0.19	0.25	0.70	0.98	0.77	0.96	0.27	0.32	0.96	0.79	0.93	0.63	0.93	0.99	0.52	0.49	0.18	0.49	0.09	0.08	0.92
P C	P h e	0.09	0.20	0.02	-0.12	-0.01	0.04	0.463**	-0.08	-0.09	0.02	0.01	-0.12	0.07	0.05	0.03	0.00	0.03	0.04	-0.14	-0.15	0.04
S		0.49	0.11	0.85	0.34	0.94	0.74	0.00	0.52	0.46	0.85	0.91	0.33	0.57	0.68	0.81	0.99	0.81	0.75	0.27	0.21	0.73
PC	A n t h	0.11	0.15	0.10	-0.03	0.03	0.11	0.19	0.06	0.07	0.12	0.01	-0.13	0.03	0.12	0.09	0.05	0.05	0.13	-0.15	-0.13	0.08
S		0.39	0.22	0.40	0.81	0.80	0.39	0.13	0.62	0.59	0.33	0.91	0.29	0.82	0.35	0.49	0.67	0.70	0.28	0.24	0.30	0.53
PC	Fluranth	0.05	0.20	-0.05	-0.13	0.00	0.01	0.15	0.00	0.05	0.06	-0.01	-0.08	0.07	0.12	0.04	-0.02	-0.02	0.10	-0.08	-0.01	0.04
S		0.68	0.11	0.71	0.29	0.99	0.92	0.23	0.97	0.68	0.65	0.94	0.49	0.59	0.34	0.74	0.87	0.84	0.44	0.50	0.91	0.77
PC	P y r	0.01	0.09	-0.13	-0.17	-0.05	-0.06	0.10	-0.03	0.02	-0.03	-0.05	-0.06	0.05	0.04	-0.01	-0.10	-0.10	0.06	-0.05	-0.08	-0.03
S		0.96	0.45	0.29	0.16	0.66	0.61	0.40	0.82	0.88	0.81	0.67	0.62	0.72	0.74	0.92	0.41	0.44	0.63	0.71	0.52	0.81
PC	Chrys	-0.22	-0.20	-0.297*	-0.293*	-0.302*	-0.301*	-0.18	-0.22	-0.272*	-0.271*	-0.259*	-0.24	-0.24	-0.24	-0.265*	-0.312*	-0.288*	-0.22	-0.285*	-0.270*	-0.309*
S		0.07	0.11	0.01	0.02	0.01	0.01	0.15	0.07	0.03	0.03	0.03	0.05	0.05	0.05	0.03	0.01	0.02	0.07	0.02	0.03	0.01
PC	Benzanth	-0.13	-0.10	-0.21	-0.251*	-0.17	-0.19	-0.06	-0.03	-0.07	-0.16	-0.17	-0.13	-0.10	-0.10	-0.13	-0.21	-0.18	-0.04	-0.10	-0.12	-0.16
S		0.29	0.44	0.08	0.04	0.18	0.13	0.62	0.80	0.57	0.19	0.17	0.31	0.43	0.43	0.31	0.09	0.14	0.75	0.43	0.34	0.20
PC	Benzbfluranth	-0.23	-0.20	-0.338**	-0.287*	-0.278*	-0.289*	-0.17	-0.15	-0.21	-0.285*	-0.298*	-0.271*	-0.20	-0.20	-0.21	-0.296*	-0.244*	-0.17	-0.245*	-0.20	-0.285*
S		0.06	0.11	0.01	0.02	0.02	0.02	0.18	0.21	0.09	0.02	0.01	0.03	0.11	0.10	0.08	0.01	0.05	0.18	0.05	0.10	0.02
PC	Benzkfluranth	-0.08	-0.04	-0.21	-0.242*	-0.21	-0.20	-0.10	-0.14	-0.13	-0.20	-0.19	-0.18	-0.12	-0.13	-0.16	-0.19	-0.19	-0.06	-0.17	-0.20	-0.18
S		0.51	0.74	0.08	0.05	0.09	0.11	0.41	0.25	0.29	0.11	0.13	0.16	0.35	0.31	0.20	0.13	0.12	0.61	0.18	0.11	0.14
PC	Benzapyr	-0.05	-0.01	-0.17	-0.22	-0.22	-0.19	-0.10	-0.17	-0.14	-0.19	-0.16	-0.16	-0.14	-0.13	-0.17	-0.16	-0.20	-0.05	-0.16	-0.20	-0.17
S		0.70	0.94	0.16	0.07	0.08	0.11	0.41	0.17	0.27	0.12	0.18	0.19	0.27	0.28	0.17	0.20	0.10	0.70	0.20	0.10	0.16
PC	Indeno123cdpyr	-0.03	0.01	-0.17	-0.23	-0.18	-0.16	-0.14	-0.12	-0.09	-0.13	-0.12	-0.15	-0.11	-0.07	-0.11	-0.08	-0.13	0.02	-0.10	-0.07	-0.12
S		0.81	0.90	0.18	0.06	0.14	0.19	0.26	0.32	0.45	0.29	0.34	0.22	0.39	0.60	0.36	0.55	0.31	0.84	0.44	0.60	0.33
P C	benzghiperyl	-0.10	-0.06	-0.20	-0.23	-0.17	-0.17	-0.17	-0.08	-0.10	-0.14	-0.16	-0.18	-0.12	-0.08	-0.10	-0.09	-0.11	-0.01	-0.11	-0.06	-0.14
S		0.44	0.66	0.11	0.06	0.17	0.18	0.17	0.50	0.44	0.27	0.20	0.15	0.35	0.54	0.43	0.45	0.36	0.92	0.38	0.64	0.26
PC	dibenzahanth	-0.03	0.01	-0.12	-0.22	-0.18	-0.16	-0.13	-0.16	-0.13	-0.15	-0.14	-0.16	-0.12	-0.10	-0.13	-0.06	-0.11	0.00	-0.13	-0.13	-0.13
S		0.79	0.95	0.32	0.08	0.14	0.21	0.29	0.19	0.29	0.23	0.25	0.18	0.33	0.44	0.31	0.61	0.37	1.00	0.29	0.29	0.29
P C	totalpah	-0.15	-0.09	-0.282*	-0.306*	-0.260*	-0.255*	-0.12	-0.16	-0.18	-0.23	-0.24	-0.24	-0.17	-0.15	-0.19	-0.244*	-0.23	-0.10	-0.22	-0.21	-0.24
S		0.23	0.46	0.02	0.01	0.03	0.04	0.34	0.18	0.15	0.06	0.05	0.05	0.18	0.21	0.12	0.05	0.06	0.43	0.07	0.09	0.05
PC	T O C	-0.10	-0.11	-0.11	0.01	-0.09	-0.14	-0.03	-0.248*	-0.379*	-0.21	-0.251*	-0.19	-0.04	-0.15	-0.19	-0.17	-0.01	-0.20	-0.20	0.00	-0.17
S		0.42	0.36	0.38	0.95	0.47	0.27	0.78	0.04	0.00	0.08	0.04	0.12	0.72	0.24	0.13	0.16	0.93	0.10	0.11	0.98	0.18

Table 17: Upper Marsh Pearson Product Moment Correlations – PCBs versus PAHs

		Ace	Flu	Phe	Anth	Fluranth	Pyr	Chrys	Benzanth	Benzbfluranth	Benzkfluranth	Benzapy	Indeno123cdpyr	benzoghiperyl	dibenzahanth	totalpah	TOC
PC	Ace	1.00	**0.746****	0.498**	0.548**	0.477**	0.343**	0.19	0.23	0.20	0.492**	0.508**	0.434**	0.378**	0.500**	0.424**	-
S			**0.00**	0.00	0.00	0.00	0.00	0.13	0.06	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.73
PC	Flu	**0.746****	1.00	0.488**	0.21	0.287*	0.22	0.493**	0.13	0.239*	0.370**	0.448**	0.352**	0.242*	0.429**	0.414**	0.04
S		**0.00**		0.00	0.08	0.02	0.07	0.00	0.31	0.05	0.00	0.00	0.00	0.05	0.00	0.00	0.74
PC	Phe	0.498**	0.488**	1.00	0.547**	0.400**	0.350**	0.09	0.16	0.14	0.363**	0.367**	0.296*	0.250*	0.430**	0.326**	0.12
S		0.00	0.00		0.00	0.00	0.00	0.47	0.20	0.24	0.00	0.00	0.01	0.04	0.00	0.01	0.32
PC	Anth	0.548**	0.21	0.547**	1.00	0.405**	0.345**	-0.07	0.245*	0.274*	0.372**	0.342**	0.364**	0.397**	0.438**	0.354**	-
S		0.00	0.08	0.00		0.00	0.00	0.56	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.38
PC	Fluoranth	0.477**	0.287*	0.400**	0.405**	1.00	**0.903****	0.18	0.673**	0.453**	0.586**	0.521**	0.501**	0.489**	0.487**	0.641**	-
S		0.00	0.02	0.00	0.00		**0.00**	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.85
PC	Pyr	0.343**	0.22	0.350**	0.345**	**0.903****	1.00	0.22	**0.821****	0.559**	0.657**	0.576**	0.552**	0.563**	0.521**	**0.724****	-
S		0.00	0.07	0.00	0.00	**0.00**		0.07	**0.00**	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**	0.66
PC	Chrys	0.19	0.493**	0.09	-0.07	0.18	0.22	1.00	0.253*	0.609**	0.23	0.250*	0.338**	0.363**	0.293*	0.577**	-
S		0.13	0.00	0.47	0.56	0.15	0.07		0.04	0.00	0.06	0.04	0.00	0.00	0.02	0.00	0.55
PC	Benzaanth	0.23	0.13	0.16	0.245*	0.673**	**0.821****	0.253*	1.00	**0.717****	**0.772****	0.650**	0.651**	0.675**	0.573**	**0.808****	-
S		0.06	0.31	0.20	0.04	0.00	**0.00**	0.04		**0.00**	**0.00**	0.00	0.00	0.00	0.00	**0.00**	0.31
PC	Benzbfluranth	0.20	0.239*	0.14	0.274*	0.453**	0.559**	0.609**	**0.717****	1.00	0.653**	0.576**	**0.748****	**0.817****	0.634**	**0.906****	-
S		0.10	0.05	0.24	0.02	0.00	0.00	0.00	**0.00**		0.00	0.00	**0.00**	**0.00**	0.00	**0.00**	0.29
PC	Benzkfluranth	0.492**	0.370**	0.363**	0.372**	0.586**	0.657**	0.23	**0.772****	0.653**	1.00	**0.962****	**0.896****	**0.853****	**0.900****	**0.873****	0.00
S		0.00	0.00	0.00	0.00	0.00	0.00	0.06	**0.00**	0.00		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.99
PC	Benzapyr	0.508**	0.448**	0.367**	0.342**	0.521**	0.576**	0.250*	0.650**	0.576**	**0.962****	1.00	**0.890****	**0.810****	**0.926****	**0.827****	0.02
S		0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	0.85
PC	Indeno123cdpyr	0.434**	0.352**	0.296*	0.364**	0.501**	0.552**	0.338**	0.651**	**0.748****	**0.896****	**0.890****	1.00	**0.965****	**0.935****	**0.897****	-
S		0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	0.89
PC	benzoghiperyl	0.378**	0.242*	0.250*	0.397**	0.489**	0.563**	0.363**	0.675**	**0.817****	**0.853****	**0.810****	**0.965****	1.00	**0.885****	**0.906****	-
S		0.00	0.05	0.04	0.00	0.00	0.00	0.00	0.00	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	0.47
PC	dibenzahanth	0.500**	0.429**	0.430**	0.438**	0.487**	0.521**	0.293*	0.573**	0.634**	**0.900****	**0.926****	**0.935****	**0.885****	1.00	**0.840****	0.05
S		0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	0.70
PC	totalpah	0.424**	0.414**	0.326**	0.354**	0.641**	**0.724****	0.577**	**0.808****	**0.906****	**0.873****	**0.827****	**0.897****	**0.906****	**0.840****	1.00	-
S		0.00	0.00	0.01	0.00	0.00	**0.00**	0.00	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		0.54
PC	TOC	-0.04	0.04	0.12	-0.11	-0.02	-0.05	-0.07	-0.12	-0.13	0.00	0.02	-0.02	-0.09	0.05	-0.08	1.00
S		0.73	0.74	0.32	0.38	0.85	0.66	0.55	0.31	0.29	0.99	0.85	0.89	0.47	0.70	0.54	

Table 18: Upper Marsh Pearson Product Moment Correlations – PAHs versus PAHs

		Ace	Flu	Phen	Anth	Fluranth	Pyr	Chrys	Benzanth	Benzbfluranth	Benzkfluranth	Benzapyr	Indeno123cdpyr	benzghiperyl	dibenzahanth	totalpah	TOC
P C	χ L F	0.16	0.294*	0.316**	-0.03	0.22	0.11	0.24	-0.04	-0.09	-0.01	-0.03	-0.15	-0.17	-0.08	0.01	-0.06
S		0.19	0.01	0.01	0.78	0.07	0.35	0.05	0.77	0.48	0.96	0.80	0.22	0.16	0.52	0.94	0.62
P C	F D %	-0.05	0.01	0.07	-0.01	-0.21	-0.21	0.01	-0.15	-0.07	-0.04	-0.03	0.03	-0.02	0.03	-0.07	0.21
S		0.68	0.91	0.56	0.93	0.08	0.09	0.90	0.21	0.59	0.72	0.84	0.83	0.84	0.80	0.59	0.09
PC	S I R M	0.18	0.339**	0.313**	-0.01	0.23	0.11	0.239*	-0.04	-0.07	0.00	-0.03	-0.15	-0.17	-0.08	0.02	-0.04
S		0.13	0.00	0.01	0.91	0.06	0.37	0.05	0.78	0.59	0.99	0.83	0.23	0.17	0.54	0.88	0.77
PC	χ A R M	0.09	0.17	0.240*	0.02	0.13	0.10	0.23	0.02	0.02	0.05	0.02	-0.05	-0.04	-0.01	0.08	0.285*
S		0.45	0.18	0.05	0.85	0.28	0.42	0.06	0.86	0.90	0.67	0.89	0.71	0.75	0.91	0.54	0.02
PC	χARM/SIRM	-0.07	-0.14	-0.01	0.04	-0.04	0.03	0.05	0.07	0.09	0.08	0.06	0.10	0.13	0.06	0.08	0.384**
S		0.58	0.26	0.93	0.77	0.74	0.84	0.69	0.57	0.47	0.52	0.63	0.43	0.30	0.63	0.50	0.00
PC	SIRM/χLF	0.16	0.284*	0.02	0.11	0.07	0.01	0.06	0.01	0.09	0.02	0.01	-0.03	-0.01	-0.02	0.05	0.04
S		0.20	0.02	0.87	0.39	0.58	0.93	0.65	0.95	0.48	0.87	0.92	0.83	0.91	0.89	0.70	0.77
PC	χARM/χLF	-0.03	-0.08	0.00	0.06	-0.03	0.03	0.06	0.08	0.10	0.09	0.06	0.09	0.12	0.06	0.09	0.373**
S		0.79	0.51	0.97	0.65	0.84	0.81	0.63	0.53	0.40	0.49	0.61	0.46	0.32	0.65	0.45	0.00
PC	H I R M	-0.01	0.16	0.08	-0.09	0.07	0.07	0.13	-0.05	-0.11	-0.12	-0.11	-0.22	-0.23	-0.16	-0.08	-0.07
S		0.94	0.18	0.51	0.48	0.54	0.57	0.27	0.66	0.37	0.35	0.37	0.07	0.05	0.20	0.51	0.60
PC	HARD %	-0.239*	-0.304*	-0.322**	-0.06	-0.22	-0.08	-0.20	0.02	0.02	-0.07	-0.04	0.04	0.04	0.00	-0.07	0.02
S		0.05	0.01	0.01	0.62	0.07	0.53	0.10	0.88	0.90	0.55	0.75	0.77	0.72	0.99	0.57	0.86
PC	A R M	0.09	0.17	0.240*	0.02	0.13	0.10	0.23	0.02	0.02	0.05	0.02	-0.05	-0.04	-0.01	0.08	0.285*
S		0.45	0.18	0.05	0.85	0.28	0.42	0.06	0.86	0.90	0.67	0.89	0.71	0.75	0.91	0.54	0.02
PC	SIRM/ARM	0.05	0.12	-0.03	-0.07	0.04	-0.01	-0.07	-0.05	-0.08	-0.08	-0.06	-0.09	-0.12	-0.07	-0.08	-0.372*
S		0.69	0.32	0.81	0.57	0.76	0.92	0.58	0.70	0.54	0.51	0.62	0.47	0.34	0.58	0.51	0.00
P C	S o f t	0.22	0.373**	0.330**	0.00	0.241*	0.13	0.23	0.00	-0.01	0.05	0.02	-0.10	-0.11	-0.03	0.07	-0.10
S		0.07	0.00	0.01	0.99	0.05	0.29	0.06	1.00	0.95	0.68	0.86	0.40	0.35	0.81	0.59	0.42
PC	-20mT	0.23	0.278*	0.23	0.09	0.18	0.12	0.09	0.09	0.17	0.18	0.15	0.08	0.11	0.13	0.17	-0.23
S		0.06	0.02	0.06	0.45	0.15	0.35	0.47	0.45	0.17	0.15	0.22	0.52	0.38	0.31	0.16	0.06
P C	-300mT	0.239*	0.304*	0.322**	0.06	0.22	0.08	0.20	-0.02	-0.02	0.07	0.04	-0.04	-0.04	0.00	0.07	-0.02
S		0.05	0.01	0.01	0.62	0.07	0.53	0.10	0.88	0.90	0.55	0.75	0.77	0.72	0.99	0.57	0.86

Table 19: Upper Marsh Pearson Product Moment Correlations – PAHs versus Magnetics

		Ace	Flu	Phe	Anth	Fluoranth	Pyr	Chrys	Benzanthr	Benzbfluranth	Benzkfluranth	Benzoapyr	Indeno123cdpyr	benzoghiperyl	dibenzahanthr	totalpah	TOC
P C	Mean	-0.19	-0.287*	-0.245*	-0.18	-0.11	-0.06	-0.318**	-0.01	-0.04	-0.01	0.01	0.08	0.06	0.01	-0.08	0.17
S		0.11	0.02	0.04	0.15	0.39	0.61	0.01	0.94	0.77	0.94	0.91	0.53	0.65	0.92	0.51	0.16
P C	Sorting	-0.273*	-0.303*	-0.292*	-0.19	-0.21	-0.12	-0.291*	-0.06	-0.06	-0.08	-0.05	0.02	0.00	-0.05	-0.13	0.322**
S		0.02	0.01	0.02	0.12	0.08	0.35	0.02	0.61	0.62	0.51	0.67	0.90	1.00	0.66	0.28	0.01
P C	Skewness	-0.241*	-0.290*	-0.337**	-0.11	-.276*	-0.16	-0.24	-0.06	-0.01	-0.06	-0.03	0.05	0.06	-0.02	-0.10	0.330**
S		0.05	0.02	0.00	0.37	0.02	0.20	0.05	0.63	0.91	0.65	0.79	0.69	0.64	0.85	0.42	0.01
PC	Kurtosis	0.08	0.16	0.08	-0.03	0.05	-0.03	0.06	-0.10	-0.21	-0.19	-0.18	-0.253*	-0.289*	-0.22	-0.17	-0.22
S		0.52	0.20	0.51	0.79	0.71	0.79	0.61	0.40	0.09	0.12	0.13	0.04	0.02	0.07	0.17	0.08
PC	%Sand	-0.240*	-0.324**	-0.295*	-0.16	-0.18	-0.10	-0.361**	-0.02	-0.04	-0.02	0.01	0.08	0.06	0.02	-0.10	0.24
S		0.05	0.01	0.01	0.18	0.14	0.41	0.00	0.86	0.76	0.90	0.93	0.51	0.60	0.90	0.42	0.05
PC	%Mud	0.240*	0.324**	0.295*	0.16	0.18	0.10	0.361**	0.02	0.04	0.02	-0.01	-0.08	-0.06	-0.02	0.10	-0.24
S		0.05	0.01	0.01	0.18	0.14	0.41	0.00	0.86	0.76	0.90	0.93	0.51	0.60	0.90	0.42	0.05
PC	%vcoarse sand	-0.13	-0.13	-0.11	-0.12	0.02	-0.01	-0.06	-0.06	-0.09	-0.10	-0.10	-0.09	-0.09	-0.12	-0.10	0.12
S		0.29	0.28	0.37	0.32	0.90	0.95	0.63	0.61	0.45	0.42	0.44	0.44	0.45	0.32	0.43	0.32
PC	%coarse sand	-0.21	-0.24	-0.21	-0.19	-0.10	-0.05	-0.15	-0.06	-0.07	-0.10	-0.09	-0.04	-0.05	-0.11	-0.11	0.267*
S		0.09	0.05	0.08	0.12	0.44	0.66	0.21	0.65	0.60	0.42	0.49	0.75	0.71	0.38	0.37	0.03
PC	%medium sand	-0.21	-0.250*	-0.246*	-0.20	-0.13	-0.05	-0.18	-0.01	0.00	-0.05	-0.03	0.04	0.03	-0.04	-0.06	0.266*
S		0.09	0.04	0.04	0.10	0.28	0.71	0.14	0.96	0.97	0.68	0.80	0.72	0.79	0.72	0.62	0.03
PC	%fine sand	-0.255*	-0.293*	-0.302*	-0.15	-0.269*	-0.17	-0.357**	-0.08	-0.06	-0.06	-0.01	0.06	0.04	0.01	-0.13	0.24
S		0.04	0.02	0.01	0.23	0.03	0.17	0.00	0.50	0.63	0.66	0.92	0.61	0.73	0.93	0.27	0.05
PC	%vfine sand	-0.01	-0.23	-0.09	0.04	0.14	0.08	-0.403**	0.17	0.01	0.22	0.19	0.18	0.17	0.19	0.05	-0.08
S		0.97	0.06	0.48	0.74	0.24	0.50	0.00	0.16	0.90	0.07	0.11	0.14	0.16	0.12	0.68	0.50
PC	%vcoarse silt	0.19	0.20	0.244*	0.04	0.265*	0.15	0.13	0.06	-0.02	0.05	0.03	-0.04	-0.05	0.01	0.06	-0.381**
S		0.12	0.11	0.04	0.75	0.03	0.23	0.27	0.62	0.88	0.68	0.78	0.73	0.66	0.94	0.60	0.00
P C	%coarse silt	0.291*	0.368**	0.329**	0.16	0.20	0.09	0.352**	0.00	0.02	0.02	0.00	-0.07	-0.07	0.00	0.10	-0.286*
S		0.02	0.00	0.01	0.20	0.10	0.45	0.00	0.97	0.86	0.87	0.99	0.58	0.59	0.97	0.43	0.02
PC	%medium silt	0.15	0.20	0.11	0.19	-0.01	0.00	0.332**	0.01	0.10	0.02	-0.01	-0.01	0.03	0.01	0.10	0.00
S		0.23	0.10	0.39	0.13	0.93	0.97	0.01	0.95	0.41	0.89	0.97	0.91	0.81	0.94	0.40	0.97
P C	%fine silt	0.06	0.12	0.05	0.14	-0.05	-0.01	0.260*	-0.01	0.08	-0.01	-0.03	-0.03	0.02	-0.02	0.07	0.08
S		0.65	0.33	0.69	0.26	0.66	0.93	0.03	0.97	0.50	0.94	0.81	0.82	0.90	0.87	0.59	0.50
PC	%vfine silt	0.06	0.17	0.14	0.13	-0.01	0.02	0.261*	-0.03	0.03	-0.06	-0.07	-0.11	-0.08	-0.07	0.03	0.09
S		0.65	0.17	0.24	0.29	0.92	0.90	0.03	0.80	0.82	0.65	0.55	0.39	0.53	0.57	0.84	0.46
PC	%clay	0.05	0.23	0.242*	0.09	0.04	0.04	0.261*	-0.05	-0.04	-0.10	-0.12	-0.18	-0.18	-0.12	-0.02	0.07
		0.69	0.06	0.05	0.48	0.75	0.72	0.03	0.66	0.74	0.40	0.34	0.14	0.13	0.31	0.86	0.58

Table 20: Upper Marsh Pearson Product Moment Correlations – PAHs versus Grain Size

		χ L F	F D %	S I R M	χ A R M	χARM/SIRM	SIRM/χLF	χARM/XLF	H I R M	HARD%	A R M	SIRM/ARM	S o f t	-20mT	-300mT
PC	χ L F	1.00	0.00	**0.981**	0.643	-0.13	0.11	-0.11	0.621	**-0.785**	0.643	0.08	**0.940**	0.340	**0.785**
S			0.97	**0.00**	0.00	0.27	0.36	0.39	0.00	**0.00**	0.00	0.52	**0.00**	0.00	**0.00**
PC	F D %	0.00	1.00	-0.06	0.16	0.291	-0.355	0.21	-0.22	-0.08	0.16	-0.313	-0.10	-0.15	0.08
S		0.97		0.60	0.19	0.02	0.00	0.08	0.07	0.53	0.19	0.01	0.42	0.23	0.53
PC	S I R M	**0.981**	-0.06	1.00	0.681	-0.10	0.301	-0.04	0.646	**-0.803**	0.681	0.05	**0.957**	0.345	**0.803**
S		**0.00**	0.60		0.00	0.41	0.01	0.73	0.00	**0.00**	0.00	0.70	**0.00**	0.00	**0.00**
PC	χ A R M	0.643	0.16	0.681	1.00	0.648	0.325	0.682	0.369	-0.670	**1.000**	-0.685	0.587	0.05	0.670
S		0.00	0.19	0.00		0.00	0.01	0.00	0.00	0.00	**0.00**	0.00	0.00	0.70	0.00
PC	χARM/SIRM	-0.13	0.291	-0.10	0.648	1.00	0.15	**0.985**	-0.21	-0.12	0.648	**-0.983**	-0.18	-0.262	0.12
S		0.27	0.02	0.41	0.00		0.23	**0.00**	0.09	0.32	0.00	**0.00**	0.15	0.03	0.32
PC	SIRM/χLF	0.11	-0.355	0.301	0.325	0.15	1.00	.313	0.24	-0.280	0.325	-0.15	0.290	0.12	0.280
S		0.36	0.00	0.01	0.01	0.23		0.01	0.05	0.02	0.01	0.23	0.02	0.34	0.02
PC	χARM/χLF	-0.11	0.21	-0.04	0.682	**0.985**	0.313	1.00	-0.15	-0.17	0.682	**-0.969**	-0.12	-0.23	0.17
S		0.39	0.08	0.73	0.00	**0.00**	0.01		0.21	0.18	0.00	**0.00**	0.34	0.06	0.18
PC	H I R M	0.621	-0.22	0.646	0.369	-0.21	0.24	-0.15	1.00	-0.08	0.369	0.17	0.592	0.14	0.08
S		0.00	0.07	0.00	0.00	0.09	0.05	0.21		0.50	0.00	0.16	0.00	0.24	0.50
PC	HARD %	**-0.785**	-0.08	**-0.803**	-0.670	-0.12	-0.280	-0.17	-0.08	1.00	-0.670	0.16	**-0.778**	-0.310	**-1.000**
S		**0.00**	0.53	**0.00**	0.00	0.32	0.02	0.18	0.50		0.00	0.18	**0.00**	0.01	**0.00**
PC	A R M	0.643	0.16	0.681	**1.000**	0.648	0.325	0.682	0.369	-0.670	1.00	-0.685	0.587	0.05	0.670
S		0.00	0.19	0.00	**0.00**	0.00	0.01	0.00	0.00	0.00		0.00	0.00	0.70	0.00
PC	SIRM/ARM	0.08	-0.313	0.05	-0.685	**-0.983**	-0.15	**-0.969**	0.17	0.16	-0.685	1.00	0.13	0.241	-0.16
S		0.52	0.01	0.70	0.00	**0.00**	0.23	**0.00**	0.16	0.18	0.00		0.30	0.05	0.18
PC	S o f t	**0.940**	-0.10	**0.957**	0.587	-0.18	0.290	-0.12	0.592	**-0.778**	0.587	0.13	1.00	0.598	**0.778**
S		**0.00**	0.42	**0.00**	0.00	0.15	0.02	0.34	0.00	**0.00**	0.00	0.30		0.00	**0.00**
PC	-20mT	0.340	-0.15	0.345	0.05	-0.262	0.12	-0.23	0.14	-0.310	0.05	0.241	0.598	1.00	0.310
S		0.00	0.23	0.00	0.70	0.03	0.34	0.06	0.24	0.01	0.70	0.05	0.00		0.01
PC	-300mT	**0.785**	0.08	**0.803**	0.670	0.12	0.280	0.17	0.08	**-1.000**	0.670	-0.16	**0.778**	0.310	1.00
S		**0.00**	0.53	**0.00**	0.00	0.32	0.02	0.18	0.50	**0.00**	0.00	0.18	**0.00**	0.01	

Table 21: Upper Marsh Pearson Product Moment Correlations – Magnetics versus Magnetics

		χ l f	FD%	S I R M	χARM	χARM/SIRM	SIRM/χLF	χARM/χLF	H I R M	HARD%	A R M	SIRM/ARM	S o f t	-20mT	-300mT
PC	Mean	-0.598**	0.15	-0.608**	-0.448**	0.10	-0.16	0.06	-0.557**	0.378**	-0.448**	-0.02	-0.570**	-0.19	-0.378**
S		0.00	0.23	0.00	0.00	0.43	0.19	0.64	0.00	0.00	0.00	0.89	0.00	0.12	0.00
PC	Sorting	**-0.740****	0.17	**-0.718****	-0.331**	0.325**	-0.05	0.297*	-0.499**	0.535**	-0.331**	-0.263*	**-0.716****	-0.351**	-0.535**
S		**0.00**	0.16	**0.00**	0.01	0.01	0.71	0.01	0.00	0.00	0.01	0.03	**0.00**	0.00	0.00
PC	Skewness	**-0.820****	0.12	**-0.773****	-0.242*	0.468**	0.06	0.454**	-0.490**	0.585**	-0.242*	-0.422**	**-0.783****	-0.406**	-0.585**
S		**0.00**	0.34	**0.00**	0.05	0.00	0.61	0.00	0.00	0.00	0.05	0.00	**0.00**	0.00	0.00
PC	Kurtosis	0.601**	-0.09	0.602**	0.276*	-0.23	0.17	-0.19	0.401**	-0.499**	0.276*	0.18	0.541**	0.09	0.499**
S		0.00	0.45	0.00	0.02	0.06	0.17	0.13	0.00	0.00	0.02	0.13	0.00	0.46	0.00
PC	% Sand	**-0.754****	0.15	**-0.749****	-0.478**	0.17	-0.13	0.14	-0.583**	0.533**	-0.478**	-0.10	**-0.722****	-0.284*	-0.533**
S		**0.00**	0.22	**0.00**	0.00	0.16	0.30	0.27	0.00	0.00	0.00	0.41	**0.00**	0.02	0.00
PC	% Mud	**0.754****	-0.15	**0.749****	0.478**	-0.17	0.13	-0.14	0.583**	-0.533**	0.478**	0.10	**0.722****	0.284*	0.533**
S		**0.00**	0.22	**0.00**	0.00	0.16	0.30	0.27	0.00	0.00	0.00	0.41	**0.00**	0.02	0.00
PC	%coarse sand	-0.13	-0.04	-0.13	0.06	0.247*	0.03	0.243*	-0.09	0.08	0.06	-0.20	-0.12	-0.01	-0.08
S		0.28	0.74	0.30	0.65	0.04	0.83	0.05	0.49	0.52	0.65	0.10	0.35	0.91	0.52
PC	%coarse sand	-0.431**	0.13	-0.412**	-0.09	0.364**	0.02	0.351**	-0.349**	0.240*	-0.09	-0.301*	-0.413**	-0.21	-0.240*
S		0.00	0.29	0.00	0.46	0.00	0.84	0.00	0.00	0.05	0.46	0.01	0.00	0.08	0.05
PC	%medium sand	-0.586**	0.18	-0.565**	-0.243*	0.309*	0.00	0.292*	-0.427**	0.390**	-0.243*	-0.247*	-0.562**	-0.286*	-0.390**
S		0.00	0.15	0.00	0.05	0.01	0.98	0.02	0.00	0.00	0.05	0.04	0.00	0.02	0.00
PC	%fine sand	**-0.809****	0.15	**-0.804****	-0.511**	0.16	-0.15	0.12	-0.582**	0.601**	-0.511**	-0.10	**-0.780****	-0.317**	-0.601**
S		**0.00**	0.21	**0.00**	0.00	0.19	0.21	0.34	0.00	0.00	0.00	0.43	**0.00**	0.01	0.00
PC	%vfine sand	-0.253*	-0.05	-0.287*	-0.487**	-0.323**	-0.23	-0.353**	-0.347**	0.17	-0.487**	0.358**	-0.22	0.08	-0.17
S		0.04	0.71	0.02	0.00	0.01	0.06	0.00	0.00	0.16	0.00	0.00	0.07	0.53	0.16
PC	%coarse silt	**0.734****	-0.13	0.676**	0.10	-0.527**	-0.12	-0.521**	0.354**	-0.557**	0.10	0.505**	**0.705****	0.409**	0.557**
S		**0.00**	0.28	0.00	0.44	0.00	0.35	0.00	0.00	0.00	0.44	0.00	**0.00**	0.00	0.00
PC	%coarse silt	**0.811****	-0.14	**0.796****	0.405**	-0.292*	0.10	-0.255*	0.537**	-0.612**	0.405**	0.22	**0.778****	0.335**	0.612**
S		**0.00**	0.25	**0.00**	0.00	0.02	0.41	0.04	0.00	0.00	0.00	0.07	**0.00**	0.01	0.00
PC	%medium silt	0.242*	-0.10	0.285*	0.468**	0.257*	0.260*	0.298*	0.334**	-0.17	0.468**	-0.316**	0.239*	0.01	0.17
S		0.05	0.41	0.02	0.00	0.03	0.03	0.01	0.01	0.17	0.00	0.01	0.05	0.94	0.17
PC	%fine silt	0.09	-0.06	0.14	0.432**	0.348**	0.24	0.380**	0.292*	-0.02	0.432**	-0.399**	0.09	-0.08	0.02
S		0.46	0.61	0.26	0.00	0.00	0.05	0.00	0.02	0.90	0.00	0.00	0.48	0.52	0.90
PC	%vfine silt	0.249*	-0.04	0.288*	0.489**	0.260*	0.22	0.291*	0.432**	-0.09	0.489**	-0.324**	0.23	-0.04	0.09
S		0.04	0.72	0.02	0.00	0.03	0.07	0.02	0.00	0.46	0.00	0.01	0.06	0.77	0.46
PC	% clay	0.463**	-0.02	0.487**	0.520**	0.10	0.19	0.13	0.583**	-0.22	0.520**	-0.18	0.412**	0.01	0.22
		0.00	0.90	0.00	0.00	0.42	0.13	0.28	0.00	0.08	0.00	0.14	0.00	0.92	0.08

Table 22: Upper Marsh Pearson Product Moment Correlations – Magnetics versus Grain Size

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
PC	Si	1.00	0.676**	0.23	0.687**	-0.19	-0.679**	-0.522**	-0.25	-0.548**	-0.325*	-0.21	-0.500**	0.574**	-0.554**	-0.21	0.27	-0.07	-0.12	-0.538**	0.07	-0.16
S			0.00	0.18	0.00	0.26	0.00	0.00	0.14	0.00	0.05	0.21	0.00	0.00	0.00	0.22	0.10	0.67	0.49	0.00	0.68	0.35
PC	Al	0.676**	1.00	0.23	0.462**	0.08	-0.403*	-0.27	-0.12	-0.26	-0.22	-0.08	-0.358*	0.338*	-0.345*	-0.03	0.11	-0.18	-0.08	-0.387*	0.28	-0.08
S		0.00		0.17	0.00	0.65	0.01	0.10	0.49	0.13	0.18	0.64	0.03	0.04	0.04	0.88	0.53	0.29	0.63	0.02	0.09	0.63
PC	Ti	0.23	0.23	1.00	0.12	**0.727****	0.23	0.04	-0.03	0.04	0.23	0.13	-0.05	0.20	-0.01	-0.02	0.02	0.12	-0.18	-0.20	-0.08	0.05
S		0.18	0.17		0.48	**0.00**	0.17	0.83	0.86	0.84	0.18	0.43	0.77	0.23	0.94	0.89	0.89	0.47	0.29	0.23	0.83	0.76
PC	Ca	0.687**	0.462**	0.12	1.00	-0.23	-0.32	-0.12	-0.05	-0.13	-0.540**	-0.358*	0.09	0.10	-0.27	0.333*	0.00	-0.03	-0.05	-0.07	-0.07	-0.333*
S		0.00	0.00	0.48		0.17	0.05	0.49	0.79	0.43	0.00	0.03	0.59	0.54	0.10	0.04	0.99	0.85	0.78	0.67	0.89	0.04
PC	K	-0.19	0.08	**0.727****	-0.23	1.00	0.598**	0.14	0.32	0.389*	0.591**	0.577**	0.00	-0.19	0.32	0.09	0.05	0.22	-0.21	0.06	0.20	0.15
S		0.26	0.65	**0.00**	0.17		0.00	0.40	0.06	0.02	0.00	0.00	0.98	0.25	0.05	0.61	0.75	0.18	0.20	0.71	0.22	0.38
PC	Fe	-0.679**	-0.403*	0.23	-0.32	0.598**	1.00	0.612**	0.576**	**0.729****	0.463**	0.399*	0.543**	-0.610**	0.679**	0.356*	-0.24	0.31	-0.09	0.565**	-0.04	0.11
S		0.00	0.01	0.17	0.05	0.00		0.00	0.00	**0.00**	0.00	0.01	0.00	0.00	0.00	0.03	0.15	0.06	0.58	0.00	0.81	0.52
PC	Mn	-0.522**	-0.27	0.04	-0.12	0.14	0.612**	1.00	0.17	0.465**	-0.07	-0.17	**0.712****	-0.31	0.373*	0.552**	**-0.785****	0.11	-0.14	0.673**	-0.348*	-0.08
S		0.00	0.10	0.83	0.49	0.40	0.00		0.32	0.00	0.69	0.33	**0.00**	0.06	0.02	0.00	**0.00**	0.50	0.41	0.00	0.03	0.63
PC	S	-0.25	-0.12	-0.03	-0.05	0.32	0.576**	0.17	1.00	0.689**	0.564**	0.563**	0.13	-0.602**	0.437**	0.16	0.08	0.13	-0.26	0.19	0.516**	-0.07
S		0.14	0.49	0.86	0.79	0.06	0.00	0.32		0.00	0.00	0.00	0.43	0.00	0.01	0.36	0.65	0.46	0.12	0.26	0.00	0.66
PC	Cl	-0.548**	-0.26	0.04	-0.13	0.389*	**0.729****	0.465**	0.689**	1.00	0.423**	0.378*	0.396*	**-0.739****	0.519**	0.28	-0.12	0.18	-0.06	0.489**	0.23	0.02
S		0.00	0.13	0.84	0.43	0.02	**0.00**	0.00	0.00		0.01	0.02	0.02	**0.00**	0.00	0.09	0.49	0.27	0.71	0.00	0.16	0.92
PC	Pb	-.325*	-0.22	0.23	-0.540**	0.591**	0.463**	-0.07	0.564**	0.423**	1.00	**0.855****	-0.21	-0.383*	0.409*	-0.334*	0.18	0.25	-0.16	-0.05	0.453**	0.377*
S		0.05	0.18	0.18	0.00	0.00	0.00	0.69	0.00	0.01		**0.00**	0.21	0.02	0.01	0.04	0.30	0.13	0.35	0.78	0.00	0.02
PC	Zn	-0.21	-0.08	0.13	-0.358*	0.577**	0.399*	-0.17	0.563**	0.378*	**0.855****	1.00	-0.19	-0.429**	0.375*	-0.21	0.22	0.30	-0.24	-0.06	0.506**	0.20
S		0.21	0.64	0.43	0.03	0.00	0.01	0.33	0.00	0.02	**0.00**		0.26	0.01	0.02	0.22	0.19	0.07	0.15	0.74	0.00	0.23
PC	Br	-0.500**	-0.358*	-0.05	0.09	0.00	0.543**	**0.712****	0.13	0.396*	-0.21	-0.19	1.00	-0.502**	0.524**	0.580**	-0.482**	0.08	0.06	**0.749****	-0.29	-0.21
S		0.00	0.03	0.77	0.59	0.98	0.00	**0.00**	0.43	0.02	0.21	0.26		0.00	0.00	0.00	0.00	0.66	0.74	**0.00**	0.08	0.22
PC	Zr	0.574**	0.338*	0.20	0.10	-0.19	-0.610**	-0.31	-0.602**	**-0.739****	-0.383*	-0.429**	-0.502**	1.00	-0.557**	-0.31	0.16	-0.07	-0.05	-0.606**	-0.31	0.03
S		0.00	0.04	0.23	0.54	0.25	0.00	0.06	0.00	**0.00**	0.02	0.01	0.00		0.00	0.06	0.36	0.66	0.75	0.00	0.06	0.88
PC	Rb	-0.554**	-0.345*	-0.01	-0.27	0.32	0.679**	0.373*	0.437**	0.519**	.409*	0.375*	0.524**	-0.557**	1.00	0.03	-0.14	0.10	0.15	0.488**	0.01	0.03
S		0.00	0.04	0.94	0.10	0.05	0.00	0.02	0.01	0.00	0.01	0.02	0.00	0.00		0.86	0.42	0.57	0.38	0.00	0.95	0.88
PC	Sr	-0.21	-0.03	-0.02	0.333*	0.09	0.356*	0.552**	0.16	0.28	-0.334*	-0.21	0.580**	-0.31	0.03	1.00	-0.394*	0.07	-0.345*	0.517**	-0.09	-0.22
S		0.22	0.88	0.89	0.04	0.61	0.03	0.00	0.36	0.09	0.04	0.22	0.00	0.06	0.86		0.02	0.66	0.04	0.00	0.61	0.19
PC	Cr	0.27	0.11	0.02	0.00	0.05	-0.24	**-0.785****	0.08	-0.12	0.18	0.22	-0.482**	0.16	-0.14	-0.394*	1.00	0.03	0.20	-0.422**	0.413*	0.11
S		0.10	0.53	0.89	0.99	0.75	0.15	**0.00**	0.65	0.49	0.30	0.19	0.00	0.36	0.42	0.02		0.86	0.25	0.01	0.01	0.53
PC	Ni	-0.07	-0.18	0.12	-0.03	0.22	0.31	0.11	0.13	0.18	0.25	0.30	0.08	-0.07	0.10	0.07	0.03	1.00	-0.17	0.07	-0.15	0.364*
S		0.67	0.29	0.47	0.85	0.18	0.06	0.50	0.46	0.27	0.13	0.07	0.66	0.66	0.57	0.66	0.86		0.31	0.67	0.39	0.03
PC	Y	-0.12	-0.08	-0.18	-0.05	-0.21	-0.09	-0.14	-0.26	-0.06	-0.16	-0.24	0.06	-0.05	0.15	-0.345*	0.20	-0.17	1.00	0.01	-0.17	-0.01
S		0.49	0.63	0.29	0.78	0.20	0.58	0.41	0.12	0.71	0.35	0.15	0.74	0.75	0.38	0.04	0.25	0.31		0.94	0.32	0.94
PC	LOI	-0.538**	-0.387*	-0.20	-0.07	0.06	0.565**	0.673**	0.19	0.489**	-0.05	-0.06	**0.749****	-0.606**	0.488**	0.517**	-0.422**	0.07	0.01	1.00	-0.13	0.00
S		0.00	0.02	0.23	0.67	0.71	0.00	0.00	0.26	0.00	0.78	0.74	**0.00**	0.00	0.00	0.00	0.01	0.67	0.94		0.43	1.00
PC	Cd	0.07	0.28	-0.08	-0.07	0.20	-0.04	-0.348*	0.516**	0.23	0.453**	0.506**	-0.29	-0.31	0.01	-0.09	0.413*	-0.15	-0.17	-0.13	1.00	0.03
S		0.68	0.09	0.63	0.69	0.22	0.81	0.03	0.00	0.16	0.00	0.00	0.08	0.06	0.95	0.61	0.01	0.39	0.32	0.43		0.85
PC	Hg	-0.16	-0.08	0.05	-0.333*	0.15	0.11	-0.08	-0.07	0.02	0.377*	0.20	-0.21	0.03	0.03	-0.22	0.11	0.364*	-0.01	0.00	0.03	1.00
S		0.35	0.63	0.76	0.04	0.38	0.52	0.63	0.66	0.92	0.02	0.23	0.22	0.88	0.88	0.19	0.53	0.03	0.94	1.00	0.85	

Table 23: Channel Core Pearson Product Moment Correlations – Elements versus Elements

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
PC	χ L F	0.377*	0.19	0.18	-0.14	0.18	-0.25	-0.626**	0.23	-0.16	0.511**	0.518**	-0.638**	0.25	-0.16	-0.555**	0.626**	0.09	-0.13	-0.594**	0.413*	0.16
S		0.02	0.27	0.28	0.40	0.30	0.13	0.00	0.18	0.35	0.00	0.00	0.00	0.13	0.33	0.00	0.00	0.59	0.46	0.00	0.01	0.35
PC	F D %	-0.22	0.01	0.01	0.05	0.14	0.30	0.346*	0.08	0.28	0.04	0.09	0.341*	-0.23	0.12	0.382*	-0.30	0.20	-0.05	0.28	0.06	0.26
S		0.20	0.98	0.95	0.76	0.40	0.07	0.04	0.62	0.13	0.82	0.60	0.04	0.17	0.49	0.02	0.07	0.24	0.79	0.12	0.71	0.12
PC	S I R M	0.383*	0.24	0.16	-0.12	0.20	-0.27	-0.615**	0.22	-0.14	0.512**	0.545**	-0.616**	0.21	-0.18	-0.493**	0.584**	0.04	-0.18	-0.573**	0.448**	0.13
S		0.02	0.16	0.36	0.48	0.24	0.10	0.00	0.20	0.39	0.00	0.00	0.00	0.22	0.28	0.00	0.00	0.82	0.28	0.00	0.01	0.45
PC	χ A R M	-0.678**	-0.421**	0.11	-0.379*	0.496**	0.653**	0.445**	0.16	0.541**	0.383*	0.375*	0.503**	-0.661**	0.524**	0.30	-0.28	0.29	-0.04	0.660**	0.01	0.21
S		0.00	0.01	0.51	0.02	0.00	0.00	0.01	0.34	0.00	0.02	0.02	0.00	0.00	0.00	0.07	0.09	0.09	0.83	0.00	0.97	0.21
PC	χARM/SIRM	-0.684**	-0.417**	0.00	-0.20	0.23	0.587**	0.641**	-0.05	0.436**	-0.05	-0.07	0.690**	-0.548**	0.464**	0.464**	-0.505**	0.17	0.10	0.770**	-0.27	0.07
S		0.00	0.01	0.98	0.23	0.18	0.00	0.00	0.77	0.01	0.76	0.66	0.00	0.00	0.00	0.00	0.00	0.30	0.55	0.00	0.10	0.69
PC	SIRM/χLF	0.09	0.25	-0.09	0.08	0.12	-0.13	-0.07	0.01	0.04	0.11	0.22	-0.03	-0.17	-0.11	0.16	-0.07	-0.22	-0.27	-0.02	0.24	-0.10
S		0.58	0.14	0.60	0.66	0.49	0.44	0.68	0.94	0.82	0.51	0.19	0.86	0.31	0.51	0.33	0.69	0.20	0.11	0.91	0.14	0.57
PC	χARM/χLF	-0.679**	-0.389*	-0.02	-0.20	0.25	0.575**	0.632**	-0.04	0.447**	-0.03	-0.03	0.667**	-0.582**	0.452**	0.485**	-0.515**	0.14	0.07	0.772**	-0.23	0.06
S		0.00	0.02	0.92	0.23	0.14	0.00	0.00	0.80	0.01	0.88	0.84	0.00	0.00	0.00	0.00	0.00	0.39	0.69	0.00	0.16	0.73
PC	H I R M	0.378*	0.378*	-0.01	0.31	-0.10	-0.412*	-0.12	-0.360*	-0.27	-0.26	-0.12	-0.10	0.26	-0.32	0.08	-0.10	-0.20	-0.23	-0.22	-0.10	-0.11
S		0.02	0.02	0.95	0.08	0.55	0.01	0.48	0.03	0.10	0.12	0.49	0.56	0.12	0.05	0.82	0.55	0.23	0.17	0.18	0.56	0.53
PC	H A R D %	0.21	0.27	-0.07	.370*	-0.19	-0.29	0.16	-0.480**	-0.22	-0.505**	-0.379*	0.18	0.19	-0.25	0.31	-0.352*	-0.21	-0.13	0.03	-0.32	-0.18
S		0.20	0.10	0.69	0.02	0.27	0.08	0.34	0.00	0.19	0.00	0.02	0.29	0.27	0.14	0.07	0.03	0.22	0.43	0.84	0.05	0.30
PC	A R M	-0.678**	-0.421**	0.11	-0.379*	0.496**	0.653**	0.445**	0.16	0.541**	0.383*	0.375*	0.503**	-0.661**	0.524**	0.30	-0.28	0.29	-0.04	0.660**	0.01	0.21
S		0.00	0.01	0.51	0.02	0.00	0.00	0.01	0.34	0.00	0.02	0.02	0.00	0.00	0.00	0.07	0.09	0.09	0.83	0.00	0.97	0.21
PC	SIRM/ARM	0.660**	0.439**	-0.02	0.14	-0.23	-0.635**	-0.718**	-0.01	-0.457**	0.06	0.08	-0.733**	0.543**	-0.460**	-0.544**	0.579**	-0.18	-0.04	-0.789**	0.30	-0.03
S		0.00	0.01	0.91	0.39	0.17	0.00	0.00	0.96	0.00	0.75	0.66	0.00	0.00	0.00	0.00	0.00	0.27	0.83	0.00	0.08	0.84
PC	S o f t	0.468**	0.361*	0.23	0.03	0.14	-0.27	-0.507**	0.08	-0.19	0.29	0.341*	-0.540**	0.360*	-0.24	-0.338*	0.501**	0.05	-0.14	-0.623**	0.25	0.04
S		0.00	0.03	0.17	0.86	0.39	0.11	0.00	0.65	0.25	0.08	0.04	0.00	0.03	0.15	0.04	0.00	0.77	0.41	0.00	0.14	0.81
PC	- 2 0 m T	0.357*	0.370*	0.22	0.26	-0.04	-0.14	-0.04	-0.21	-0.20	-0.26	-0.22	-0.12	0.442**	-0.21	0.10	0.07	0.01	0.02	-0.361*	-0.23	-0.14
S		0.03	0.02	0.19	0.12	0.80	0.41	0.81	0.21	0.23	0.12	0.18	0.46	0.01	0.20	0.54	0.70	0.94	0.93	0.03	0.16	0.42
PC	- 3 0 0 m T	-0.21	-0.27	0.07	-0.370*	0.19	0.29	-0.16	0.480**	0.22	0.505**	0.379*	-0.18	-0.19	0.25	-0.31	0.352*	0.21	0.13	-0.03	0.32	0.18
S		0.20	0.10	0.69	0.02	0.27	0.08	0.34	0.00	0.19	0.00	0.02	0.29	0.27	0.14	0.07	0.03	0.22	0.43	0.84	0.05	0.30

Table 24: Channel Core Pearson Product Moment Correlations – Elements verus Magnetics

		Si	Al	Ti	Ca	K	Fe	Mn	S	Cl	Pb	Zn	Br	Zr	Rb	Sr	Cr	Ni	Y	LOI	Cd	Hg
P C	Mean	0.31	0.17	0.00	0.09	-0.02	-0.17	-0.390*	0.515**	-0.03	0.27	0.27	-0.457**	0.11	-0.24	-0.24	0.356*	-0.01	-0.21	-0.505**	0.514**	-0.05
S		0.06	0.31	0.98	0.59	0.93	0.32	0.02	0.00	0.84	0.10	0.10	0.00	0.50	0.14	0.15	0.03	0.96	0.21	0.00	0.00	0.75
P C	Sorting	-0.522**	-0.529**	0.05	-0.23	0.335*	0.430**	0.19	0.27	0.30	0.31	0.29	0.29	-0.528**	0.24	0.29	-0.20	0.32	-0.15	0.359*	0.03	0.13
S		0.00	0.00	0.75	0.17	0.04	0.01	0.26	0.11	0.07	0.06	0.08	0.08	0.00	0.16	0.08	0.23	0.05	0.38	0.03	0.84	0.44
P C	Skewness	-0.656**	-0.562**	0.06	-0.16	0.25	0.550**	0.502**	0.00	0.419**	-0.01	-0.04	0.626**	-0.508**	0.459**	0.415*	-0.368*	0.16	0.09	0.672**	-0.31	-0.03
S		0.00	0.00	0.71	0.35	0.13	0.00	0.00	0.99	0.01	0.96	0.83	0.00	0.00	0.00	0.01	0.03	0.33	0.61	0.00	0.06	0.84
PC	Kurtosis	.415*	0.31	0.01	0.00	-0.02	-0.29	-0.539**	0.373*	-0.10	0.329*	0.30	-0.602**	0.25	-0.15	-0.551**	0.496**	-0.17	-0.11	-0.578**	0.530**	-0.02
S		0.01	0.06	0.96	1.00	0.92	0.08	0.00	0.02	0.55	0.05	0.07	0.00	0.14	0.38	0.00	0.00	0.33	0.53	0.00	0.00	0.90
PC	%Sand	0.04	-0.08	0.01	0.02	0.10	0.04	-0.22	0.567**	0.11	0.32	0.32	-0.24	-0.12	-0.15	-0.02	0.21	0.13	-0.24	-0.28	0.452**	-0.03
S		0.81	0.64	0.97	0.92	0.56	0.80	0.19	0.00	0.54	0.06	0.06	0.15	0.49	0.38	0.90	0.21	0.46	0.14	0.10	0.01	0.88
PC	%Mud	-0.04	0.08	-0.01	-0.02	-0.10	-0.04	0.22	-0.567**	-0.11	-0.32	-0.32	0.24	0.12	0.15	0.02	-0.21	-0.13	0.24	0.28	-0.452**	0.03
S		0.81	0.64	0.97	0.92	0.56	0.80	0.19	0.00	0.54	0.06	0.06	0.15	0.49	0.38	0.90	0.21	0.46	0.14	0.10	0.01	0.88
PC	%coarse	0.22	0.00	0.12	-0.04	0.11	-0.18	-0.32	0.14	-0.18	0.17	0.15	-0.391*	0.21	-0.04	-0.334*	0.27	-0.03	-0.21	-0.28	0.14	-0.01
S		0.20	1.00	0.48	0.79	0.52	0.29	0.05	0.40	0.28	0.33	0.36	0.02	0.21	0.82	0.04	0.11	0.84	0.22	0.10	0.40	0.98
PC	%medium	0.20	-0.02	0.16	-0.01	0.13	-0.22	-0.424**	0.26	-0.22	0.27	0.21	-0.426**	0.18	-0.11	-0.32	0.32	0.01	-0.10	-0.491**	0.30	-0.04
S		0.24	0.91	0.33	0.95	0.45	0.20	0.01	0.12	0.19	0.10	0.21	0.01	0.30	0.51	0.06	0.05	0.96	0.57	0.00	0.07	0.83
PC	%fine	-0.24	-0.27	-0.01	-0.13	0.27	0.367*	-0.05	0.722**	0.438**	0.503**	0.503**	-0.02	-0.460**	0.11	0.08	0.11	0.24	-0.28	0.07	0.470**	0.08
S		0.15	0.11	0.97	0.46	0.11	0.03	0.79	0.00	0.01	0.00	0.00	0.92	0.00	0.50	0.63	0.53	0.15	0.09	0.69	0.00	0.64
PC	%fine/c	0.24	0.15	-0.08	0.19	-0.18	-0.19	-0.17	0.24	-0.14	-0.06	-0.02	-0.24	0.16	-0.385*	0.06	0.14	-0.01	-0.13	-0.379*	0.26	-0.13
S		0.15	0.38	0.64	0.26	0.29	0.25	0.32	0.15	0.41	0.73	0.89	0.16	0.33	0.02	0.72	0.42	0.95	0.43	0.02	0.13	0.46
PC	%mean	0.649**	0.561**	-0.05	0.14	-0.23	-0.536**	-0.525**	0.02	-0.382*	0.03	0.05	-0.648**	0.520**	-0.389*	-0.500**	0.415*	-0.20	-0.07	-0.665**	0.326*	0.01
S		0.00	0.00	0.78	0.42	0.17	0.00	0.00	0.92	0.02	0.84	0.77	0.00	0.00	0.02	0.00	0.01	0.24	0.70	0.00	0.05	0.93
PC	%sand	0.09	0.18	-0.06	0.06	-0.15	-0.01	0.12	-0.12	0.11	-0.11	-0.14	0.08	0.07	0.27	-0.21	-0.04	-0.20	0.21	0.15	-0.18	-0.06
S		0.58	0.29	0.71	0.73	0.38	0.97	0.48	0.47	0.50	0.52	0.40	0.62	0.69	0.11	0.21	0.83	0.23	0.21	0.37	0.30	0.70
P C	%coarse	-0.432**	-0.30	0.04	-0.06	0.06	0.31	0.517**	-0.410*	0.16	-0.30	-0.30	0.599**	-0.21	0.31	0.388*	-0.422**	0.05	0.20	0.606**	-0.547**	-0.02
S		0.01	0.07	0.83	0.71	0.71	0.06	0.00	0.01	0.35	0.07	0.07	0.00	0.20	0.06	0.02	0.01	0.79	0.23	0.00	0.00	0.89
PC	%medsil	-0.441**	-0.32	0.04	-0.10	0.09	0.28	0.464**	-0.442**	0.11	-0.28	-0.25	0.567**	-0.23	0.27	0.385*	-0.412*	0.08	0.18	0.583**	-0.520**	0.02
S		0.01	0.06	0.83	0.56	0.59	0.09	0.00	0.01	0.53	0.12	0.13	0.00	0.17	0.10	0.02	0.01	0.84	0.29	0.00	0.00	0.90
P C	%fine/f	-0.449**	-0.325*	0.04	-0.15	0.12	0.27	.410*	-0.431**	0.09	-0.19	-0.19	0.523**	-0.26	0.27	0.342*	-0.388*	0.08	0.16	0.556**	-0.468**	0.07
S		0.01	0.05	0.82	0.37	0.47	0.10	0.01	0.01	0.59	0.26	0.26	0.00	0.12	0.11	0.04	0.02	0.64	0.34	0.00	0.00	0.70
PC	%mud	-0.391*	-0.28	0.05	-0.25	0.16	0.18	0.25	-0.449**	0.00	-0.05	-0.07	0.352*	-0.23	0.21	0.17	-0.30	0.06	0.14	0.428**	-0.362*	0.18
S		0.02	0.09	0.78	0.13	0.34	0.30	0.13	0.01	0.99	0.79	0.67	0.03	0.18	0.22	0.31	0.07	0.71	0.41	0.01	0.03	0.27
PC	%clay	0.31	0.17	0.00	0.09	-0.02	-0.17	-0.390*	0.515**	-0.03	0.27	0.27	-0.457**	0.11	-0.24	-0.24	0.356*	-0.01	-0.21	-0.505**	0.514**	-0.05
		0.06	0.31	0.98	0.59	0.93	0.32	0.02	0.00	0.84	0.10	0.10	0.00	0.50	0.14	0.15	0.03	0.96	0.21	0.00	0.00	0.75

Table 25: Channel Core Pearson Product Moment Correlations – Elements versus Grain Size

		χ L F	F D %	S I R M	χARM	χARM/SIRM	SIRM/χLF	χARM/χLF	H I R M	HARD%	A R M	SIRM/ARM	S o f t	-20mT	-300mT
P C	χ L F	1.00	-0.354*	**0.974****	-0.29	**-0.747****	0.07	**-0.736****	0.05	-0.378*	-0.29	**0.773****	**0.843****	0.14	0.378*
S			0.03	**0.00**	0.09	**0.00**	0.66	**0.00**	0.77	0.02	0.09	**0.00**	**0.00**	0.42	0.02
P C	F D %	-0.354*	1.00	-0.342*	0.32	0.378*	0.00	0.380*	-0.03	0.11	0.32	-0.454**	-0.31	-0.09	-0.11
S		0.03		0.04	0.06	0.02	1.00	0.02	0.86	0.50	0.06	0.00	0.06	0.61	0.50
PC	S I R M	**0.974****	-0.342*	1.00	-0.25	**-0.742****	0.30	**-0.700****	0.23	-0.21	-0.25	**0.768****	**0.875****	0.16	0.21
S		**0.00**	0.04		0.13	**0.00**	0.07	**0.00**	0.17	0.21	0.13	**0.00**	**0.00**	0.36	0.21
PC	χARM	-0.29	0.32	-0.25	1.00	**0.831****	0.11	**0.856****	-0.16	-0.05	**1.000****	**-0.793****	-0.370*	-0.386*	0.05
S		0.09	0.06	0.13		**0.00**	0.52	**0.00**	0.34	0.76	**0.00**	**0.00**	0.02	0.02	0.76
PC	χARM/SIRM	**-0.747****	0.378*	**-0.742****	**0.831****	1.00	-0.12	**0.990****	-0.25	0.08	**0.831****	**-0.977****	**-0.751****	-0.351*	-0.08
S		**0.00**	0.02	**0.00**	**0.00**		0.50	**0.00**	0.14	0.62	**0.00**	**0.00**	**0.00**	0.03	0.62
PC	SIRM/χLF	0.07	0.00	0.30	0.11	-0.12	1.00	0.03	**0.807****	0.659**	0.11	0.12	0.29	0.09	-0.659**
S		0.66	1.00	0.07	0.52	0.50		0.88	**0.00**	0.00	0.52	0.47	0.08	0.58	0.00
PC	χARM/χLF	**-0.736****	0.380*	**-0.700****	**0.856****	**0.990****	0.03	1.00	-0.14	0.17	**0.856****	**-0.965****	**-0.714****	-0.346*	-0.17
S		**0.00**	0.02	**0.00**	**0.00**	**0.00**	0.88		0.41	0.32	**0.00**	**0.00**	**0.00**	0.04	0.32
PC	H I R M	0.05	-0.03	0.23	-0.16	-0.25	**0.807****	-0.14	1.00	**0.900****	-0.16	0.24	0.351*	0.334*	**-0.900****
S		0.77	0.86	0.17	0.34	0.14	**0.00**	0.41		**0.00**	0.34	0.16	0.03	0.04	**0.00**
PC	HARD %	-0.378*	0.11	-0.21	-0.05	0.08	0.659**	0.17	**0.900****	1.00	-0.05	-0.10	-0.03	0.29	**-1.000****
S		0.02	0.50	0.21	0.76	0.62	0.00	0.32	**0.00**		0.76	0.54	0.87	0.09	**0.00**
PC	A R M	-0.29	0.32	-0.25	**1.000****	**0.831****	0.11	**0.856****	-0.16	-0.05	1.00	**-0.793****	-0.370*	-0.386*	0.05
S		0.09	0.06	0.13	**0.00**	**0.00**	0.52	**0.00**	0.34	0.76		**0.00**	0.02	0.02	0.76
PC	SIRM/ARM	**0.773****	-0.454**	**0.768****	**-0.793****	**-0.977****	0.12	**-0.965****	0.24	-0.10	**-0.793****	1.00	**0.745****	0.29	0.10
S		**0.00**	0.00	**0.00**	**0.00**	**0.00**	0.47	**0.00**	0.16	0.54	**0.00**		**0.00**	0.08	0.54
P C	S o f t	**0.843****	-0.31	**0.875****	-0.370*	**-0.751****	0.29	**-0.714****	0.351*	-0.03	-0.370*	**0.745****	1.00	0.612**	0.03
S		0.00	0.06	**0.00**	0.02	**0.00**	0.08	**0.00**	0.03	0.87	0.02	**0.00**		0.00	0.87
PC	-20mT	0.14	-0.09	0.16	-0.386*	-0.351*	0.09	-0.346*	0.334*	0.29	-0.386*	0.29	0.612**	1.00	-0.29
S		0.42	0.61	0.36	0.02	0.03	0.58	0.04	0.04	0.09	0.02	0.08	0.00		0.09
P C	-300mT	0.378*	-0.11	0.21	0.05	-0.08	-0.659**	-0.17	**-0.900****	**-1.000****	0.05	0.10	0.03	-0.29	1.00
S		0.02	0.50	0.21	0.76	0.62	0.00	0.32	**0.00**	**0.00**	0.76	0.54	0.87	0.09	

Table 26: Channel Core Pearson Product Moment Correlations – Magnetics versus Magnetics

		χ L F	F D %	S I R M	χ A R M	χARM/SIRM	SIRM/χLF	χARM/χLF	H I R M	HARD%	A R M	SIRM/ARM	S o f t	-20mT	-300mT
P C	Mean	0.586**	-0.23	0.559**	-0.471**	-0.659**	0.00	-0.661**	-0.07	-0.330*	-0.471**	0.627**	0.441**	0.01	0.330*
S		0.00	0.17	0.00	0.00	0.00	1.00	0.00	0.69	0.05	0.00	0.00	0.01	0.97	0.05
P C	Sorting	-0.24	0.20	-0.22	0.656**	0.564**	0.04	0.578**	-0.25	-0.17	0.656**	-0.560**	-0.377*	-0.430**	0.17
S		0.15	0.25	0.19	0.00	0.00	0.81	0.00	0.14	0.32	0.00	0.00	0.02	0.01	0.32
P C	Skewnes	-0.645**	0.28	-0.652**	**0.734****	**0.881****	-0.15	**0.868****	-0.31	-0.02	**0.734****	**-0.862****	-0.693**	-0.373*	0.02
S		0.00	0.09	0.00	**0.00**	**0.00**	0.39	**0.00**	0.06	0.91	**0.00**	**0.00**	0.00	0.02	0.91
PC	Kurtosis	0.695**	-0.414*	0.668**	-0.561**	**-0.783****	0.01	**-0.782****	-0.04	-0.353*	-0.581**	**0.802****	0.497**	-0.05	0.353*
S		0.00	0.01	0.00	0.00	**0.00**	0.95	**0.00**	0.80	0.03	0.00	**0.00**	0.00	0.76	0.03
PC	%Sand	0.382*	-0.08	0.363*	-0.15	-0.330*	0.00	-0.329*	-0.16	-0.341*	-0.15	0.29	0.22	-0.13	0.341*
S		0.02	0.64	0.03	0.38	0.05	0.98	0.05	0.34	0.04	0.38	0.08	0.18	0.45	0.04
PC	%Mud	-0.382*	0.08	-0.363*	0.15	0.330*	0.00	0.329*	0.16	0.341*	0.15	-0.29	-0.22	0.13	-.0341*
S		0.02	0.64	0.03	0.38	0.05	0.98	0.05	0.34	0.04	0.38	0.08	0.18	0.45	0.04
PC	fcoarsest	0.26	-0.29	0.23	-0.24	-0.30	-0.07	-0.31	-0.08	-0.19	-0.24	0.30	0.06	-0.22	0.19
S		0.12	0.09	0.17	0.15	0.07	0.68	0.06	0.66	0.26	0.15	0.07	0.70	0.20	0.26
PC	fcoarsest	0.478**	-0.326*	0.446**	-0.23	-0.414*	-0.05	-0.420**	-0.10	-0.31	-0.23	0.436**	0.24	-0.20	0.31
S		0.00	0.05	0.01	0.16	0.01	0.77	0.01	0.54	0.06	0.16	0.01	0.15	0.24	0.06
PC	fcoarsest	0.21	0.03	0.20	0.19	-0.01	0.01	0.00	-0.325*	-0.441**	0.19	-0.02	0.00	-0.336*	0.441**
S		0.21	0.88	0.23	0.25	0.96	0.95	0.99	0.05	0.01	0.25	0.93	0.98	0.04	0.01
PC	fcoarsest	0.30	0.00	0.29	-0.393*	-0.449**	0.01	-0.452**	0.09	-0.04	-0.393*	0.384*	0.340*	0.24	0.04
S		0.07	0.99	0.09	0.02	0.01	0.94	0.00	0.61	0.81	0.02	0.02	0.04	0.15	0.81
PC	fcoarsest	0.649**	-0.358*	0.645**	**0-.763****	**-0.892****	0.10	**-0.885****	0.25	-0.04	**-0.763****	**0.892****	0.650**	0.30	0.04
S		0.00	0.03	0.00	**0.00**	**0.00**	0.56	**0.00**	0.14	0.83	**0.00**	**0.00**	0.00	0.07	0.83
P C	fcoarsest	-0.10	-0.07	-0.13	-0.15	-0.02	-0.13	-0.04	-0.03	0.04	-0.15	0.04	-0.06	0.08	-0.04
S		0.55	0.66	0.46	0.37	0.89	0.45	0.80	0.87	0.83	0.37	0.82	0.70	0.64	0.83
PC	fmedsrtl	**-0.703****	0.30	-0.691**	0.556**	**0.790****	-0.08	**0.781****	-0.04	0.28	0.556**	**-0.773****	-0.568**	-0.05	-0.28
S		**0.00**	0.08	0.00	0.00	**0.00**	0.62	**0.00**	0.81	0.09	0.00	**0.00**	0.00	0.76	0.09
P C	fskewsrt	-0.678**	0.30	-0.654**	0.615**	**0.809****	-0.03	**0.809****	0.00	0.30	0.615**	**-0.785****	-0.556**	-0.09	-0.30
S		0.00	0.07	0.00	0.00	**0.00**	0.88	**0.00**	0.98	0.07	0.00	**0.00**	0.00	0.59	0.07
PC	fvfrsrtl	-0.625**	0.30	-0.592**	0.652**	**0.798****	0.02	**0.806****	0.01	0.28	0.652**	**-0.768****	-0.526**	-0.13	-0.28
S		0.00	0.07	0.00	0.00	**0.00**	0.89	**0.00**	0.97	0.09	0.00	**0.00**	0.00	0.43	0.09
PC	%clay	-0.462**	0.19	-0.414*	0.631**	0.683**	0.12	**0.705****	0.05	0.24	0.631**	-0.626**	-0.419**	-0.21	-0.24
		0.00	0.25	0.01	0.00	0.00	0.48	**0.00**	0.77	0.16	0.00	0.00	0.01	0.22	0.16

Table 27: Channel Core Pearson Product Moment Correlations – Magnetics versus Grain Size

		Si	Al	Ti	Ca	Mg	K	Fe	Mn	S	P	As	Ba	Br	Cd	Cr	Cu	Hg	Ni	Pb	Rb	Sr	V	Y	Zn	Zr	LOI
PC	Ii	1.00	0.549**	0.387*	0.13	0.355*	0.33	-0.14	0.01	-0.14	-0.32	0.23	0.16	-0.16	0.09	0.12	-0.03	0.17	0.09	-0.08	-0.02	0.10	0.14	0.29	0.07	0.415*	-0.490**
S			0.00	0.03	0.47	0.05	0.07	0.44	0.98	0.45	0.08	0.21	0.37	0.39	0.61	0.51	0.86	0.36	0.63	0.67	0.91	0.60	0.45	0.11	0.72	0.02	0.00
PC	Ii	0.549**	1.00	0.388*	-0.17	**0.707****	0.411*	0.29	-0.06	0.00	0.14	0.20	-0.05	-0.15	-0.09	0.24	-0.10	0.29	-0.02	-0.03	0.32	-0.20	0.12	0.384*	-0.07	0.17	-0.18
S		0.00		0.03	0.36	**0.00**	0.02	0.10	0.76	0.99	0.46	0.27	0.78	0.42	0.64	0.18	0.57	0.11	0.92	0.85	0.07	0.27	0.53	0.03	0.71	0.37	0.31
PC	Ti	0.387*	0.388*	1.00	-0.406*	0.22	**0.734****	-0.27	-0.529**	**-0.701****	-0.666**	0.02	-0.07	-0.09	-0.32	0.07	-0.19	-0.07	-0.23	-0.13	0.445*	-0.434*	-0.03	-0.02	-0.29	**0.588****	-0.03
S		0.03	0.03		0.02	0.24	**0.00**	0.14	0.00	**0.00**	0.00	0.92	0.71	0.61	0.07	0.70	0.29	0.71	0.21	0.48	0.01	0.01	0.85	0.91	0.10	0.00	0.89
PC	Ca	0.13	-0.17	-0.406*	1.00	-0.30	**-0.787****	0.398*	**0.895****	0.679**	0.34	**0.726****	**0.783****	0.18	**0.936****	0.30	**0.842****	-0.02	**0.889****	0.689**	**-0.797****	**0.963****	**0.764****	0.575**	**0.920****	-0.25	-0.477**
S		0.47	0.36	0.02		0.10	**0.00**	0.02	**0.00**	0.00	0.06	**0.00**	**0.00**	0.33	**0.00**	0.10	**0.00**	0.91	**0.00**	0.00	**0.00**	**0.00**	**0.00**	0.00	**0.00**	0.18	0.01
PC	Mg	0.355*	**0.707****	0.22	-0.30	1.00	0.412*	0.15	-0.16	0.06	0.24	-0.07	-0.368*	-0.27	-0.30	0.22	-0.32	0.14	-0.29	-0.28	0.360*	-0.30	-0.24	0.19	-0.30	0.17	0.11
S		0.05	**0.00**	0.24	0.10		0.02	0.43	0.37	0.76	0.19	0.71	0.04	0.14	0.10	0.22	0.07	0.44	0.11	0.12	0.04	0.09	0.18	0.30	0.09	0.36	0.56
PC	K	0.33	0.411*	**0.734****	**-0.787****	0.412*	1.00	-0.402*	**-0.812****	**-0.748****	-0.522**	-0.491**	-0.560**	-0.17	**-0.782****	-0.11	**-0.729****	0.07	**-0.741****	-0.660**	**0.723****	**-0.809****	-0.546**	-0.423*	**-0.787****	**0.459****	0.19
S		0.07	0.02	**0.00**	**0.00**	0.02		0.02	**0.00**	**0.00**	0.00	0.00	0.00	0.36	**0.00**	0.53	**0.00**	0.71	**0.00**	0.00	**0.00**	**0.00**	0.00	0.02	**0.00**	0.01	0.29
PC	Fe	-0.14	0.29	-0.27	0.398*	0.15	-0.402*	1.00	0.682**	**0.720****	0.645**	0.494**	0.375*	0.495**	0.498**	0.466**	0.502**	0.21	0.537**	0.29	-0.34	0.32	0.435*	0.352*	0.534**	-0.591**	0.03
S		0.44	0.10	0.14	0.02	0.43	0.02		0.00	**0.00**	0.00	0.00	0.03	0.00	0.00	0.01	0.00	0.25	0.00	0.11	0.06	0.08	0.01	0.05	0.00	0.00	0.88
PC	Mn	0.01	-0.06	-0.529**	**0.895****	-0.16	**-0.812****	0.682**	1.00	**0.870****	0.585**	0.677**	0.692**	0.32	**0.900****	0.368*	**0.804****	0.04	**0.853****	0.584**	**-0.750****	**0.857****	0.681**	0.553**	**0.887****	-0.529**	-0.30
S		0.98	0.76	0.00	**0.00**	0.37	**0.00**	0.00		**0.00**	0.00	0.00	0.00	0.07	**0.00**	0.04	**0.00**	0.83	**0.00**	0.00	**0.00**	**0.00**	0.00	0.00	**0.00**	0.00	0.09
PC	S	-0.14	0.00	**-0.701****	0.679**	0.06	**-0.748****	**0.720****	**0.870****	1.00	**0.863****	0.394*	0.357*	0.23	0.645**	0.24	0.512**	0.13	0.569**	0.355*	-0.630**	0.670**	0.390*	0.426*	0.624**	-0.626**	-0.05
S		0.45	0.99	**0.00**	0.00	0.76	**0.00**	**0.00**	**0.00**		**0.00**	0.03	0.04	0.20	0.00	0.18	0.00	0.48	0.00	0.05	0.00	0.00	0.03	0.02	0.00	0.00	0.77
PC	P	-0.32	0.14	-0.666**	0.34	0.24	-0.522**	0.645**	0.585**	**0.863****	1.00	0.10	-0.02	0.10	0.28	0.17	0.20	0.24	0.23	0.17	-0.31	0.352*	0.15	0.34	0.28	-0.657**	0.11
S		0.08	0.46	0.00	0.06	0.19	0.00	0.00	0.00	**0.00**		0.58	0.93	0.59	0.12	0.34	0.27	0.19	0.20	0.35	0.08	0.05	0.42	0.06	0.12	0.00	0.53
PC	As	0.23	0.20	0.02	**0.726****	-0.07	-0.491**	0.494**	0.677**	0.394*	0.10	1.00	**0.823****	0.18	**0.820****	0.358*	**0.879****	-0.07	**0.895****	**0.730****	-0.521**	**0.701****	**0.875****	0.640**	**0.873****	-0.08	-0.537**
S		0.21	0.27	0.92	**0.00**	0.71	0.00	0.00	0.00	0.03	0.58		**0.00**	0.31	**0.00**	0.04	**0.00**	0.69	**0.00**	**0.00**	0.00	**0.00**	**0.00**	0.00	**0.00**	0.64	0.00
PC	Ba	0.16	-0.05	-0.07	**0.783****	-0.368*	-0.560**	0.375*	0.692**	0.357*	-0.02	**0.823****	1.00	0.35	**0.864****	0.31	**0.847****	-0.10	**0.887****	0.643**	-0.621**	**0.723****	**0.810****	0.561**	**0.884****	-0.06	-0.458**
S		0.37	0.78	0.71	**0.00**	0.04	0.00	0.03	0.00	0.04	0.93	**0.00**		0.05	**0.00**	0.08	**0.00**	0.59	**0.00**	0.00	0.00	**0.00**	**0.00**	0.00	**0.00**	0.75	0.01
PC	Br	-0.16	-0.15	-0.09	0.18	-0.27	-0.17	0.495**	0.32	0.23	0.10	0.18	0.35	1.00	0.22	0.31	0.33	-0.05	0.29	-0.10	-0.32	0.03	0.12	-0.06	0.28	-0.420*	0.06
S		0.39	0.42	0.61	0.33	0.14	0.36	0.00	0.07	0.20	0.59	0.31	0.05		0.23	0.08	0.07	0.80	0.11	0.59	0.07	0.89	0.53	0.74	0.12	0.02	0.72
PC	Cd	0.09	-0.09	-0.32	**0.936****	-0.30	**-0.782****	0.498**	**0.900****	0.645**	0.28	**0.820****	**0.864****	0.22	1.00	0.31	**0.920****	-0.08	**0.963****	**0.789****	**-0.743****	**0.903****	**0.854****	0.598**	**0.976****	-0.28	-0.418*
S		0.61	0.64	0.07	**0.00**	0.10	**0.00**	0.00	**0.00**	0.00	0.12	**0.00**	**0.00**	0.23		0.08	**0.00**	0.65	**0.00**	**0.00**	0.00	**0.00**	**0.00**	0.00	**0.00**	0.12	0.02
PC	Cr	0.12	0.24	0.07	0.30	0.22	-0.11	0.466**	0.368*	0.24	0.17	0.358*	0.31	0.31	0.31	1.00	0.360*	0.00	0.364*	0.22	0.05	0.21	0.369*	0.395*	0.33	-0.22	-0.32
S		0.51	0.18	0.70	0.10	0.22	0.53	0.01	0.04	0.18	0.34	0.04	0.08	0.08	0.08		0.04	0.99	0.04	0.22	0.79	0.25	0.04	0.03	0.06	0.22	0.07
PC	Cu	-0.03	-0.10	-0.19	**0.842****	-0.32	**-0.729****	0.502**	**0.804****	0.512**	0.20	**0.879****	**0.847****	0.33	**0.920****	0.360*	1.00	-0.11	**0.957****	**0.845****	**-0.696****	**0.804****	**0.885****	**0.569****	**0.956****	-0.25	-0.448*
S		0.86	0.57	0.29	**0.00**	0.07	**0.00**	0.00	**0.00**	0.00	0.27	**0.00**	**0.00**	0.07	**0.00**	0.04		0.54	**0.00**	**0.00**	0.00	**0.00**	**0.00**	0.00	**0.00**	0.17	0.01
PC	Hg	0.17	0.29	-0.07	-0.02	0.14	0.07	0.21	0.04	0.13	0.24	-0.07	-0.10	-0.05	-0.08	0.00	-0.11	1.00	-0.11	-0.14	-0.06	-0.06	-0.06	0.24	-0.10	0.04	-0.14
S		0.36	0.11	0.71	0.91	0.44	0.71	0.25	0.83	0.48	0.19	0.69	0.59	0.80	0.65	0.99	0.54		0.56	0.44	0.76	0.75	0.75	0.19	0.58	0.84	0.45
PC	Ii	0.09	-0.02	-0.23	**0.889****	-0.29	**-0.741****	0.537**	**0.853****	0.569**	0.23	**0.895****	**0.887****	0.29	**0.963****	0.364*	**0.957****	-0.11	1.00	**0.814****	**-0.709****	**0.851****	**0.893****	0.623**	**0.993****	-0.23	-0.463**
S		0.63	0.92	0.21	**0.00**	0.11	**0.00**	0.00	**0.00**	0.00	0.20	**0.00**	**0.00**	0.11	**0.00**	0.04	**0.00**	0.56		**0.00**	**0.00**	**0.00**	**0.00**	0.00	**0.00**	0.21	0.01
PC	Pb	-0.08	-0.03	-0.13	**0.689****	-0.28	-0.660**	0.29	0.584**	0.355*	0.17	**0.730****	0.643**	-0.10	**0.789****	0.22	**0.845****	-0.14	**0.814****	1.00	-0.456**	**0.712****	**0.843****	0.605**	**0.803****	-0.10	-0.401*
S		0.67	0.85	0.48	0.00	0.12	0.00	0.11	0.00	0.05	0.35	**0.00**	0.00	0.59	**0.00**	0.22	**0.00**	0.44	**0.00**		0.01	**0.00**	**0.00**	0.00	**0.00**	0.60	0.02
PC	Rb	-0.02	0.32	0.445*	**-0.797****	0.360*	**0.723****	-0.34	**-0.750****	-0.630**	-0.31	-0.521**	-0.621**	-0.32	**-0.743****	0.05	-0.696**	-0.06	**-0.709****	-0.456**	1.00	**-0.771****	-0.553**	-0.28	**-0.751****	0.23	0.32
S		0.91	0.07	0.01	**0.00**	0.04	**0.00**	0.06	**0.00**	0.00	0.08	0.00	0.00	0.07	**0.00**	0.79	0.00	0.76	**0.00**	0.01		**0.00**	0.00	0.12	**0.00**	0.21	0.07
PC	Sr	0.10	-0.20	-0.434*	**0.963****	-0.30	**-0.809****	0.32	**0.857****	0.670**	0.352*	**0.701****	**0.723****	0.03	**0.903****	0.21	**0.804****	-0.06	**0.851****	**0.712****	**-0.771****	1.00	**0.742****	0.544**	**0.889****	-0.24	-0.488**
S		0.60	0.27	0.01	**0.00**	0.09	**0.00**	0.08	**0.00**	0.00	0.05	**0.00**	**0.00**	0.89	**0.00**	0.25	**0.00**	0.75	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	0.19	0.00
PC	V	0.14	0.12	-0.03	**0.764****	-0.24	-0.546**	0.435*	0.681**	0.390*	0.15	**0.875****	**0.810****	0.12	**0.854****	0.369*	**0.885****	-0.06	**0.893****	**0.843****	-0.553**	**0.742****	1.00	**0.612****	**0.879****	-0.13	-0.588**
S		0.45	0.53	0.85	**0.00**	0.18	0.00	0.01	0.00	0.03	0.42	**0.00**	**0.00**	0.53	**0.00**	0.04	**0.00**	0.75	**0.00**	**0.00**	0.00	**0.00**		**0.00**	**0.00**	0.48	0.00
PC	Y	0.29	0.384*	-0.02	0.575**	0.19	-0.423*	0.352*	0.553**	0.426*	0.34	0.640**	0.561**	-0.06	0.598**	0.395*	0.569**	0.24	0.623**	0.605**	-0.28	0.544**	0.612**	1.00	0.619**	0.00	-0.428*
S		0.11	0.03	0.91	0.00	0.30	0.02	0.05	0.00	0.02	0.06	0.00	0.00	0.74	0.00	0.03	0.00	0.19	0.00	0.00	0.12	0.00	0.00		0.00	0.98	0.01
PC	Zn	0.07	-0.07	-0.29	**0.920****	-0.30	**-0.787****	0.534**	**0.887****	0.624**	0.28	**0.873****	**0.884****	0.28	**0.976****	0.33	**0.956****	-0.10	**0.993****	**0.803****	**-0.751****	**0.889****	**0.879****	0.619**	1.00	-0.27	-0.445*
S		0.72	0.71	0.10	**0.00**	0.09	**0.00**	0.00	**0.00**	0.00	0.12	**0.00**	**0.00**	0.12	**0.00**	0.06	**0.00**	0.58	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.00		0.13	0.01
PC	Zr	0.415*	0.17	0.588**	-0.25	0.17	0.459**	-0.591**	-0.529**	-0.626**	-0.657**	-0.08	-0.06	-0.420*	-0.28	-0.22	-0.25	0.04	-0.23	-0.10	0.23	-0.24	-0.13	0.00	-0.27	1.00	-0.22
S		0.02	0.37	0.00	0.18	0.36	0.01	0.00	0.00	0.00	0.00	0.64	0.75	0.02	0.12	0.22	0.17	0.84	0.21	0.60	0.21	0.19	0.48	0.98	0.13		0.24
PC	LOI	-0.490**	-0.18	-0.03	-0.477**	0.11	0.19	0.03	-0.30	-0.05	0.11	-0.537**	-0.458**	0.06	-0.418*	-0.32	-0.448*	-0.14	-0.463**	-0.401*	0.32	-0.488**	-0.588**	-0.428*	-0.445*	-0.22	1.00
S		0.00	0.31	0.89	0.01	0.56	0.29	0.88	0.09	0.77	0.53	0.00	0.01	0.72	0.02	0.07	0.01	0.45	0.01	0.02	0.07	0.00	0.00	0.01	0.01	0.24	

Table 28: Speke Hall Pearson Product Moment Correlations – Elements versus Elements

		Si	Al	Ti	Ca	Mg	K	Fe	Mn	S	P	As	Ba	Br	Cd	Cr	Cu	Hg	Ni	Pb	Rb	Sr	V	Y	Zn	Zr	LOI
PC	KAPPA	0.13	0.11	0.631**	-0.23	-0.15	0.34	-0.405*	-0.508**	**-0.708****	-0.676**	0.16	0.09	-0.21	-0.16	-0.08	0.05	-0.11	-0.02	0.27	0.27	-0.22	0.21	0.00	-0.09	0.619**	-0.28
S		0.47	0.55	0.00	0.20	0.42	0.06	0.02	0.00	**0.00**	0.00	0.38	0.64	0.25	0.38	0.64	0.77	0.53	0.89	0.13	0.14	0.22	0.25	0.98	0.64	0.00	0.12
PC	χLF	0.14	0.12	0.629**	-0.20	-0.16	0.32	-0.385*	-0.483**	-0.690**	-0.664**	0.18	0.11	-0.21	-0.14	-0.06	0.08	-0.10	0.00	0.30	0.25	-0.20	0.24	0.03	-0.06	0.618**	-0.29
S		0.46	0.53	0.00	0.26	0.39	0.07	0.03	0.01	0.00	0.00	0.32	0.55	0.26	0.46	0.74	0.68	0.59	0.99	0.10	0.16	0.27	0.19	0.88	0.74	0.00	0.11
PC	FD%	0.12	0.26	-0.07	0.400*	0.06	-0.25	0.396*	0.394*	0.370*	0.32	0.26	0.32	0.12	0.34	0.401*	0.34	0.407*	0.353*	0.29	-0.23	0.30	0.397*	0.490**	0.358*	0.00	-0.15
S		0.52	0.15	0.72	0.02	0.75	0.17	0.02	0.03	0.04	0.08	0.15	0.08	0.51	0.06	0.02	0.06	0.02	0.05	0.10	0.21	0.09	0.02	0.00	0.04	1.00	0.41
PC	SIRM	0.18	0.27	0.674**	-0.34	0.02	0.463**	-0.26	-0.534**	-0.690**	-0.611**	0.11	0.00	-0.22	-0.27	0.02	-0.06	0.07	-0.13	0.12	0.382*	-0.35	0.12	0.00	-0.19	0.599**	-0.26
S		0.31	0.13	0.00	0.06	0.91	0.01	0.15	0.00	0.00	0.00	0.55	0.99	0.23	0.13	0.92	0.76	0.72	0.48	0.50	0.03	0.05	0.50	0.99	0.29	0.00	0.14
PC	χARM	0.21	0.397*	0.508**	-0.670**	0.33	0.675**	-0.19	-0.668**	-0.647**	-0.444*	-0.29	-0.378*	-0.15	-0.621**	-0.01	-0.482**	0.27	-0.519**	-0.387*	0.636**	**-0.704****	-0.34	-0.21	-0.568**	0.439*	0.02
S		0.25	0.02	0.00	0.00	0.07	0.00	0.31	0.00	0.00	0.01	0.10	0.03	0.42	0.00	0.95	0.01	0.14	0.00	0.03	0.00	**0.00**	0.06	0.25	0.00	0.01	0.89
PC	χARM/SIRM	0.10	0.26	0.15	**-0.763****	0.439*	0.638**	-0.13	-0.586**	-0.382*	-0.13	-0.652**	-0.669**	-0.01	**-0.768****	-0.09	**-0.753****	0.30	**-0.766****	**-0.778****	0.635**	**-0.796****	**-0.717****	-0.427*	**-0.772****	0.08	0.34
S		0.60	0.14	0.41	**0.00**	0.01	0.00	0.47	0.00	0.03	0.49	0.00	0.00	0.95	**0.00**	0.63	**0.00**	0.09	**0.00**	**0.00**	0.00	**0.00**	**0.00**	0.01	**0.00**	0.66	0.05
PC	SIRM/χLF	0.22	0.432*	0.28	-0.378*	0.399*	0.453**	0.22	-0.23	-0.18	-0.08	-0.13	-0.21	-0.03	-0.372*	0.23	-0.31	0.399*	-0.32	-0.399*	0.373*	-0.425*	-0.23	-0.07	-0.34	0.11	-0.06
S		0.24	0.01	0.13	0.03	0.02	0.01	0.22	0.21	0.33	0.68	0.49	0.25	0.88	0.04	0.21	0.08	0.02	0.07	0.02	0.04	0.02	0.20	0.72	0.06	0.54	0.76
PC	χARM/χLF	0.15	0.34	0.19	**-0.704****	0.464**	0.623**	-0.05	-0.532**	-0.357*	-0.13	-0.543**	-0.577**	-0.03	**-0.704****	-0.02	-0.679**	0.35	-0.685**	**-0.709****	0.608**	**-0.745****	-0.624**	-0.33	-0.697**	0.13	0.24
S		0.40	0.06	0.29	**0.00**	0.01	0.00	0.78	0.00	0.05	0.49	0.00	0.00	0.85	**0.00**	0.93	0.00	0.05	0.00	**0.00**	0.00	**0.00**	0.00	0.06	0.00	0.50	0.18
PC	HIRM	0.18	0.27	0.668**	-0.33	0.02	0.454**	-0.26	-0.527**	-0.684**	-0.606**	0.12	0.01	-0.22	-0.27	0.02	-0.05	0.07	-0.12	0.13	0.375*	-0.34	0.13	0.01	-0.18	0.596**	-0.26
S		0.32	0.13	0.00	0.06	0.92	0.01	0.16	0.00	0.00	0.00	0.52	0.98	0.23	0.14	0.92	0.79	0.71	0.51	0.47	0.03	0.05	0.47	0.95	0.31	0.00	0.14
PC	HARD %	-0.02	-0.17	-0.04	-0.16	0.03	0.27	-0.22	-0.13	-0.03	0.01	-0.489**	-0.364*	0.06	-0.31	-0.08	-0.375*	-0.05	-0.410*	-0.503**	0.14	-0.19	-0.472**	-0.462**	-0.383*	-0.11	0.20
S		0.91	0.37	0.81	0.39	0.85	0.14	0.22	0.48	0.87	0.94	0.00	0.04	0.76	0.08	0.65	0.03	0.79	0.02	0.00	0.46	0.30	0.01	0.01	0.03	0.56	0.26
PC	ARM	0.21	0.397*	0.508**	-0.670**	0.33	0.675**	-0.19	-0.668**	-0.647**	-0.444*	-0.29	-0.378*	-0.15	-0.621**	-0.01	-0.483**	0.27	-0.519**	-0.387*	0.637**	**-0.705****	-0.34	-0.21	-0.568**	0.438*	0.02
S		0.25	0.02	0.00	0.00	0.07	0.00	0.31	0.00	0.00	0.01	0.10	0.03	0.42	0.00	0.95	0.01	0.14	0.00	0.03	0.00	**0.00**	0.06	0.25	0.00	0.01	0.89
PC	SIRM/ARM	-0.03	-0.25	-0.22	**0.838****	-0.449*	**-0.710****	0.20	0.678**	0.464**	0.16	0.694**	**0.746****	0.06	**0.843****	0.09	**0.802****	-0.30	**0.834****	**0.798****	-0.693**	**0.859****	**0.755****	0.490**	**0.848****	-0.11	-0.375*
S		0.89	0.17	0.22	**0.00**	0.01	**0.00**	0.28	0.00	0.01	0.37	0.00	**0.00**	0.76	**0.00**	0.61	**0.00**	0.09	**0.00**	**0.00**	0.00	**0.00**	**0.00**	0.00	**0.00**	0.54	0.03
PC	Soft	0.16	0.11	0.594**	-0.15	-0.14	0.31	-0.351*	-0.423*	-0.656**	-0.661**	0.25	0.15	-0.19	-0.09	-0.02	0.13	-0.09	0.05	0.30	0.19	-0.14	0.28	-0.01	-0.02	0.568**	-0.389*
S		0.39	0.54	0.00	0.41	0.44	0.09	0.05	0.02	0.00	0.00	0.16	0.43	0.30	0.61	0.92	0.46	0.62	0.80	0.09	0.31	0.44	0.12	0.94	0.93	0.00	0.03
PC	-20mT	-0.12	-0.445*	-0.379*	0.576**	-0.370*	-0.521**	-0.06	0.460**	0.32	0.09	0.365*	0.393*	0.12	0.549**	-0.08	0.499**	-0.352*	0.495**	0.404*	-0.595**	0.624**	0.379*	0.00	0.514**	-0.26	-0.20
S		0.50	0.01	0.03	0.00	0.04	0.00	0.73	0.01	0.07	0.62	0.04	0.03	0.53	0.00	0.66	0.00	0.05	0.00	0.02	0.00	0.00	0.03	0.98	0.00	0.16	0.27
PC	-300mT	0.02	0.17	0.04	0.16	-0.03	-0.27	0.22	0.13	0.03	-0.01	0.489**	0.364*	-0.06	0.31	0.08	0.375*	0.05	0.410*	0.503**	-0.14	0.19	0.472**	0.462**	0.383*	0.11	-0.20
S		0.91	0.37	0.81	0.39	0.85	0.14	0.22	0.48	0.87	0.94	0.00	0.04	0.76	0.08	0.65	0.03	0.79	0.02	0.00	0.46	0.30	0.01	0.01	0.03	0.56	0.26
PC	Soft/ARM	-0.03	-0.32	-0.30	**0.836****	-0.452**	**-0.717****	0.14	0.679**	0.465**	0.15	0.666**	**0.719****	0.08	**0.834****	0.06	**0.781****	-0.34	**0.810****	**0.744****	**-0.721****	**0.866****	**0.710****	0.403*	**0.827****	-0.16	-0.372*
S		0.87	0.08	0.10	**0.00**	0.01	**0.00**	0.45	0.00	0.01	0.41	0.00	**0.00**	0.68	**0.00**	0.76	**0.00**	0.06	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.02	**0.00**	0.38	0.04
PC	Soft/FD%	0.01	0.04	-0.04	0.16	-0.13	-0.12	0.01	0.09	-0.05	-0.09	0.19	0.27	-0.16	0.19	-0.04	0.21	0.10	0.22	0.29	-0.09	0.15	0.27	0.21	0.21	0.15	-0.11
S		0.96	0.83	0.85	0.38	0.51	0.53	0.97	0.64	0.80	0.64	0.32	0.15	0.41	0.31	0.84	0.27	0.59	0.25	0.12	0.63	0.42	0.15	0.27	0.27	0.44	0.57
PC	χARM/f%	0.01	0.04	-0.04	0.16	-0.13	-0.12	0.01	0.09	-0.05	-0.09	0.19	0.27	-0.16	0.19	-0.04	0.21	0.10	0.22	0.29	-0.09	0.15	0.27	0.21	0.21	0.15	-0.11
S		0.96	0.83	0.85	0.38	0.51	0.53	0.97	0.64	0.80	0.64	0.32	0.15	0.41	0.31	0.84	0.27	0.59	0.25	0.12	0.63	0.42	0.15	0.27	0.27	0.44	0.57

Table 29: Speke Hall Pearson Product Moment Correlations – Elements versus Magnetics

		Si	Al	Ti	Ca	Mg	K	Fe	Mn	S	P	As	Ba	Br	Cd	Cr	Cu	Hg	Ni	Pb	Rb	Sr	V	Y	Zn	Zr	LOI
PC	Mean	-0.02	0.00	0.28	-0.672**	0.32	0.556**	-0.448*	**-0.726****	-0.471**	-0.29	-0.520**	-.0567**	-0.01	**-0.742****	-0.20	-0.598**	-0.26	**-0.708****	-0.523**	0.497**	-0.650**	-0.679**	-0.401*	**-0.708****	0.34	0.34
S		0.91	1.00	0.12	0.00	0.08	0.00	0.01	**0.00**	0.01	0.11	0.00	0.00	0.98	**0.00**	0.29	0.00	0.16	**0.00**	0.00	0.00	0.00	0.00	0.03	**0.00**	0.06	0.06
PC	Sorting	0.10	0.04	-0.32	0.17	0.01	-0.10	0.35	0.34	0.372*	0.33	-0.19	-0.05	0.12	0.12	0.22	-0.11	0.21	0.00	-0.14	-0.05	0.10	-0.02	0.00	0.02	-0.369*	-0.08
S		0.60	0.84	0.08	0.36	0.96	0.59	0.05	0.06	0.04	0.07	0.30	0.77	0.51	0.52	0.23	0.55	0.26	0.98	0.44	0.80	0.59	0.93	0.98	0.90	0.04	0.67
PC	Skewness	0.05	-0.16	0.11	-0.17	-0.15	0.22	-0.32	-0.366*	-0.396*	-0.376*	-0.20	-0.03	0.02	-0.23	0.15	-0.15	-0.19	-0.21	-0.08	0.30	-0.16	-0.12	-0.29	-0.21	0.22	-0.13
S		0.78	0.38	0.57	0.36	0.44	0.24	0.08	0.04	0.03	0.04	0.28	0.88	0.90	0.22	0.43	0.42	0.32	0.25	0.67	0.10	0.40	0.52	0.11	0.25	0.23	0.47
PC	Kurtosis	-0.10	-0.35	0.12	-0.29	-0.18	0.26	-0.504**	-0.512**	-0.478**	-.0498**	-0.28	-0.12	-0.12	-0.31	-0.18	-0.25	-0.416*	-0.35	-0.14	0.29	-0.24	-0.32	-0.481**	-0.34	0.28	0.13
S		0.58	0.05	0.51	0.11	0.35	0.16	0.00	0.00	0.01	0.00	0.13	0.52	0.53	0.09	0.34	0.17	0.02	0.05	0.46	0.11	0.20	0.08	0.01	0.06	0.13	0.50
PC	% Sand	-0.06	-0.02	0.365*	-0.660**	0.24	0.534**	-0.489**	**-0.763****	-0.552**	-0.371*	-0.416*	-0.482**	0.00	**-0.705****	-0.21	-0.499**	-0.31	-.0625**	-0.421*	0.472**	-0.618**	-0.578**	-0.373*	-0.636**	0.384*	0.32
S		0.74	0.90	0.04	0.00	0.19	0.00	0.01	**0.00**	0.00	0.04	0.02	0.01	0.99	**0.00**	0.27	0.00	0.09	0.00	0.02	0.01	0.00	0.00	0.04	0.00	0.03	0.08
PC	% Mud	0.06	0.02	-0.365*	0.660**	-0.24	-0.534**	0.489**	**0.763****	0.552**	0.371*	0.416*	0.482**	0.00	**0.705****	0.21	0.499**	0.31	0.625**	0.421*	-0.472**	0.618**	0.578**	0.373*	0.636**	-0.384*	-0.32
S		0.74	0.90	0.04	0.00	0.19	0.00	0.01	**0.00**	0.00	0.04	0.02	0.01	0.99	**0.00**	0.27	0.00	0.09	0.00	0.02	0.01	0.00	0.00	0.04	0.00	0.03	0.08
PC	%v coarse sand	-0.07	-0.20	0.11	-0.34	-0.02	0.31	-0.378*	-0.498**	-0.408*	-0.33	-0.385*	-0.22	0.15	-0.429*	0.11	-0.32	-0.403*	-0.401*	-0.26	0.397*	-0.34	-0.391*	-0.357*	-0.400*	0.22	0.10
S		0.71	0.27	0.56	0.06	0.90	0.09	0.04	0.00	0.02	0.07	0.03	0.23	0.42	0.02	0.57	0.08	0.02	0.03	0.16	0.03	0.06	0.03	0.05	0.03	0.23	0.60
PC	%coarse sand	0.12	-0.06	0.23	-0.651**	0.22	0.614**	-0.443*	**-0.716****	-0.492**	-0.359*	-0.645**	-0.568**	0.03	**-0.743****	-0.13	-0.698**	-0.17	**-0.774****	-0.634**	0.503**	-0.651**	-0.685**	-0.547**	**-0.763****	0.29	0.20
S		0.52	0.74	0.21	0.00	0.23	0.00	0.01	**0.00**	0.00	0.05	0.00	0.00	0.87	**0.00**	0.49	0.00	0.37	**0.00**	0.00	0.00	0.00	0.00	0.00	**0.00**	0.12	0.28
PC	%medium sand	-0.01	0.12	0.19	-0.676**	0.459**	0.547**	-0.26	-0.596**	-0.27	-0.05	-0.606**	-0.690**	0.03	**-0.762****	-0.16	-0.692**	-0.10	**-0.763****	-0.640**	0.484**	-0.682**	**-0.752****	-0.34	**-0.753****	0.17	0.407*
S		0.95	0.53	0.31	0.00	0.01	0.00	0.16	0.00	0.15	0.80	0.00	0.00	0.89	**0.00**	0.38	0.00	0.57	**0.00**	0.00	0.01	0.00	**0.00**	0.06	**0.00**	0.35	0.02
PC	%fine sand	-0.07	-0.04	0.420*	-0.451*	0.12	0.357*	-0.477**	-0.617**	-0.532**	-0.420*	-0.10	-0.22	-0.06	-0.437*	-0.25	-0.19	-0.33	-0.32	-0.13	0.27	-0.391*	-0.28	-0.18	-0.35	0.425*	0.22
S		0.71	0.84	0.02	0.01	0.53	0.05	0.01	0.00	0.00	0.02	0.58	0.24	0.76	0.01	0.17	0.30	0.07	0.08	0.50	0.14	0.03	0.13	0.34	0.06	0.02	0.23
PC	%vfine sand	-0.04	-0.08	-0.21	0.651**	-0.422*	-0.560**	0.33	0.618**	0.32	0.13	0.599**	0.646**	-0.03	**0.739****	0.16	0.674**	0.16	**0.750****	0.620**	-0.472**	0.665**	**0.734****	0.35	**0.740****	-0.23	-0.357*
S		0.82	0.68	0.25	0.00	0.02	0.00	0.07	0.00	0.08	0.47	0.00	0.00	0.89	**0.00**	0.38	0.00	0.40	**0.00**	0.00	0.01	0.00	**0.00**	0.06	**0.00**	0.22	0.05
PC	%v coarse silt	0.05	-0.01	-0.31	**0.700****	-0.32	-0.561**	0.433*	**0.742****	0.478**	0.28	0.505**	0.572**	0.00	**0.756****	0.22	0.596**	0.26	**0.704****	0.522**	-0.491**	0.666**	0.669**	0.387*	**0.708****	-0.32	-0.380*
S		0.77	0.94	0.09	**0.00**	0.08	0.00	0.01	**0.00**	0.01	0.13	0.00	0.00	0.98	**0.00**	0.23	0.00	0.16	**0.00**	0.00	0.01	0.00	0.00	0.03	**0.00**	0.08	0.03
PC	%coarse silt	0.11	0.09	-0.356*	0.574**	-0.15	-0.457**	0.534**	**0.727****	0.560**	0.405*	0.34	0.395*	0.02	0.614**	0.22	0.392*	0.388*	0.528**	0.30	-0.421*	0.518**	0.489**	0.359*	0.541**	-0.391*	-0.30
S		0.57	0.61	0.05	0.00	0.43	0.01	0.00	**0.00**	0.00	0.02	0.07	0.03	0.90	0.00	0.23	0.03	0.03	0.00	0.10	0.02	0.00	0.01	0.05	0.00	0.03	0.11
PC	%medium silt	0.06	0.03	-0.424*	0.636**	-0.17	-0.523**	0.529**	**0.792****	0.639**	0.473**	0.34	0.374*	0.00	0.656**	0.18	0.414*	0.33	0.547**	0.33	-0.463**	0.592**	0.480**	0.357*	0.570**	-0.453*	-0.26
S		0.77	0.86	0.02	0.00	0.36	0.00	0.00	**0.00**	0.00	0.01	0.06	0.04	1.00	0.00	0.33	0.02	0.07	0.00	0.07	0.01	0.00	0.01	0.05	0.00	0.01	0.16
PC	%fine silt	0.03	0.01	-0.469**	0.622**	-0.17	-0.531**	0.504**	**0.788****	0.647**	0.480**	0.30	0.359*	-0.02	0.648**	0.15	0.385*	0.31	0.525**	0.31	-0.464**	0.580**	0.436*	0.31	0.550**	-0.484**	-0.21
S		0.88	0.96	0.01	0.00	0.37	0.00	0.00	**0.00**	0.00	0.01	0.11	0.05	0.93	0.00	0.41	0.03	0.09	0.00	0.09	0.01	0.00	0.01	0.09	0.00	0.01	0.26
PC	%v fine silt	0.03	0.02	-0.380*	0.532**	-0.13	-0.420*	0.511**	0.689**	0.595**	0.448*	0.20	0.30	0.02	0.538**	0.19	0.26	0.35	0.415*	0.20	-0.397*	0.471**	0.362*	0.27	0.438*	-0.416*	-0.16
S		0.89	0.91	0.03	0.00	0.50	0.02	0.00	0.00	0.00	0.01	0.28	0.10	0.90	0.00	0.31	0.13	0.05	0.02	0.28	0.03	0.01	0.05	0.14	0.01	0.02	0.40
PC	% clay	0.07	0.02	-0.426*	0.680**	-0.16	-0.565**	0.512**	**0.794****	0.642**	0.440*	0.386*	0.433*	-0.05	0.698**	0.14	0.447*	0.35	0.597**	0.377*	-0.488**	0.633**	0.494**	0.401*	0.619**	-0.359*	-0.21
		0.71	0.91	0.02	0.00	0.40	0.00	0.00	**0.00**	0.00	0.01	0.03	0.02	0.79	0.00	0.47	0.01	0.06	0.00	0.04	0.01	0.00	0.00	0.03	0.00	0.05	0.26

Table 30: Speke Hall Pearson Product Moment Correlations – Elements versus Grain Size

		Si	Al	Ti	Ca	Mg	K	Fe	Mn	S	P	As	Ba	Br	Cd	Cr	Cu	Hg	Ni	Pb	Rb	Sr	V	Y	Zn	Zr	LOI
PC	18	0.07	-0.11	-0.12	0.31	-0.12	-0.24	-0.08	0.31	0.17	0.02	0.18	0.21	-0.16	0.376*	-0.24	0.21	-0.577**	0.34	0.29	-0.26	0.34	0.19	0.08	0.35	-0.03	0.09
S		0.73	0.57	0.54	0.10	0.51	0.20	0.68	0.10	0.38	0.92	0.34	0.27	0.41	0.04	0.19	0.26	0.00	0.07	0.11	0.17	0.06	0.31	0.68	0.06	0.88	0.64
PC	28	0.03	-0.19	0.04	0.31	-0.32	-0.21	-0.12	0.21	0.01	-0.17	0.30	0.370*	-0.06	0.405*	-0.22	0.33	-0.548**	0.417*	0.373*	-0.29	0.32	0.29	0.03	0.406*	0.06	0.04
S		0.88	0.30	0.84	0.10	0.08	0.28	0.52	0.27	0.98	0.36	0.11	0.04	0.74	0.03	0.25	0.08	0.00	0.02	0.04	0.11	0.08	0.12	0.87	0.03	0.77	0.82
PC	52	-0.07	-0.15	-0.02	0.17	-0.28	-0.17	-0.03	0.16	0.08	-0.02	0.13	0.21	0.08	0.25	-0.22	0.24	-0.408*	0.25	0.26	-0.26	0.20	0.10	-0.10	0.25	-0.15	0.15
S		0.71	0.44	0.91	0.37	0.13	0.36	0.88	0.39	0.67	0.90	0.50	0.27	0.68	0.19	0.25	0.21	0.03	0.19	0.16	0.17	0.30	0.60	0.59	0.17	0.44	0.44
PC	49	0.00	-0.12	-0.19	0.33	-0.31	-0.25	0.07	0.34	0.27	0.16	0.06	0.20	0.13	0.25	-0.12	0.18	-0.25	0.26	0.19	-0.32	0.35	0.13	0.05	0.29	-0.13	-0.01
S		0.99	0.52	0.30	0.08	0.10	0.19	0.72	0.07	0.15	0.41	0.74	0.29	0.48	0.18	0.52	0.35	0.18	0.17	0.32	0.09	0.06	0.50	0.79	0.12	0.48	0.98
PC	47	-0.01	-0.01	-0.19	0.577**	-0.12	-0.402*	0.22	0.526**	0.28	0.14	0.426*	0.36	-0.01	0.517**	0.407*	0.471**	-0.25	0.594**	0.444*	-0.32	0.534**	0.522**	0.23	0.574**	-0.01	-0.36
S		0.95	0.94	0.31	0.00	0.54	0.03	0.25	0.00	0.13	0.45	0.02	0.05	0.95	0.00	0.03	0.01	0.19	0.00	0.01	0.08	0.00	0.00	0.22	0.00	0.96	0.05
PC	44	-0.22	-0.22	-0.06	0.31	-0.25	-0.28	0.12	0.29	0.18	0.03	0.28	0.27	-0.12	0.389*	-0.04	0.29	-0.510**	0.383*	0.36	-0.26	0.379*	0.367*	-0.06	0.390*	-0.08	0.04
S		0.23	0.25	0.75	0.09	0.19	0.13	0.51	0.12	0.35	0.88	0.14	0.14	0.52	0.03	0.82	0.12	0.00	0.04	0.05	0.16	0.04	0.05	0.75	0.03	0.67	0.83
PC	66	0.02	-0.25	-0.14	0.538**	-0.411*	-0.427*	-0.08	0.383*	0.10	-0.03	0.394*	0.385*	0.14	0.428*	0.00	0.525**	-0.11	0.547**	0.406*	-0.535**	0.571**	0.35	0.21	0.547**	0.10	-0.365*
S		0.94	0.18	0.45	0.00	0.02	0.02	0.69	0.04	0.59	0.89	0.03	0.04	0.47	0.02	0.99	0.00	0.57	0.00	0.03	0.00	0.00	0.06	0.26	0.00	0.60	0.05
PC	101	0.01	-0.18	-0.12	0.575**	-0.363*	-0.454*	-0.04	0.451*	0.21	0.02	0.397*	0.560**	0.00	0.602**	-0.10	0.536**	-0.514**	0.635**	0.543**	-0.486**	0.596**	0.479**	0.25	0.644**	0.07	-0.16
S		0.95	0.35	0.51	0.00	0.05	0.01	0.81	0.01	0.26	0.91	0.03	0.00	0.98	0.00	0.59	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.18	0.00	0.71	0.41
PC	118	-0.13	-0.29	0.14	0.25	-0.467**	-0.17	-0.12	0.07	-0.13	-0.33	0.27	0.449*	-0.03	0.380*	-0.13	0.34	-0.484**	0.386*	0.385*	-0.26	0.28	0.364*	-0.15	0.364*	0.17	-0.04
S		0.49	0.12	0.47	0.18	0.01	0.37	0.52	0.70	0.49	0.07	0.14	0.01	0.88	0.04	0.51	0.06	0.01	0.04	0.04	0.16	0.13	0.05	0.44	0.05	0.37	0.83
PC	153	-0.23	-0.12	0.05	0.15	-0.23	-0.11	0.02	0.12	0.00	-0.02	-0.04	0.17	-0.06	0.23	0.01	0.18	-0.453*	0.21	0.29	-0.10	0.15	0.18	-0.16	0.20	0.00	0.20
S		0.22	0.52	0.78	0.42	0.22	0.57	0.91	0.51	0.98	0.92	0.84	0.36	0.76	0.23	0.96	0.35	0.01	0.26	0.12	0.58	0.42	0.35	0.41	0.29	0.99	0.30
PC	105	0.05	0.07	0.23	0.24	-0.01	0.00	-0.09	0.06	-0.14	-0.22	0.424*	0.530**	-0.13	0.34	0.00	0.34	-0.474**	0.371*	0.364*	-0.10	0.22	0.36	0.10	0.35	0.24	-0.10
S		0.80	0.73	0.23	0.20	0.96	0.99	0.65	0.75	0.46	0.23	0.02	0.00	0.48	0.06	0.99	0.06	0.01	0.04	0.05	0.60	0.25	0.05	0.59	0.06	0.20	0.60
PC	141	-0.07	-0.14	0.02	0.391*	-0.21	-0.32	0.06	0.29	0.10	-0.09	0.605**	0.599**	0.07	0.497**	-0.05	0.506**	-0.552**	0.594**	0.444*	-0.31	0.382*	0.431*	0.23	0.579**	0.04	-0.07
S		0.72	0.46	0.93	0.03	0.27	0.08	0.77	0.12	0.62	0.65	0.00	0.00	0.72	0.01	0.77	0.00	0.00	0.00	0.01	0.09	0.04	0.02	0.23	0.00	0.84	0.71
PC	138	0.01	-0.17	0.04	0.465**	-0.380*	-0.21	-0.16	0.25	-0.02	-0.15	0.25	0.516**	-0.08	0.483**	-0.05	0.433*	-0.32	0.443*	0.475**	-0.35	0.430*	0.399*	0.07	0.446*	0.11	-0.12
S		0.94	0.38	0.83	0.01	0.04	0.26	0.39	0.19	0.93	0.43	0.18	0.00	0.68	0.01	0.81	0.02	0.08	0.01	0.01	0.06	0.02	0.03	0.71	0.01	0.57	0.54
PC	183	0.10	-0.18	0.08	0.527**	-0.36	-0.31	-0.07	0.35	0.09	-0.14	0.450*	0.594**	-0.01	0.584**	-0.14	0.508**	-0.516**	0.590**	0.508**	-0.413*	0.514**	0.468**	0.26	0.591**	0.17	-0.15
S		0.60	0.35	0.66	0.00	0.05	0.10	0.71	0.06	0.63	0.46	0.01	0.00	0.95	0.00	0.45	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.17	0.00	0.36	0.43
PC	128	-0.07	-0.15	0.12	0.390*	-0.374*	-0.23	-0.07	0.23	-0.05	-0.20	0.378*	0.509**	-0.06	0.492**	0.01	0.486**	-0.550**	0.542**	0.524**	-0.30	0.385*	0.495**	0.04	0.513**	0.16	-0.12
S		0.70	0.43	0.52	0.03	0.04	0.22	0.73	0.23	0.78	0.29	0.04	0.00	0.76	0.01	0.96	0.01	0.00	0.00	0.00	0.11	0.04	0.01	0.82	0.00	0.40	0.52
PC	156	-0.05	0.00	0.20	0.34	-0.08	-0.12	0.14	0.23	-0.01	-0.13	0.522**	0.502**	-0.08	0.476**	0.17	0.450*	-0.521**	0.516**	0.473**	-0.13	0.32	0.499**	0.11	0.479**	0.12	-0.14
S		0.81	1.00	0.30	0.07	0.67	0.51	0.46	0.23	0.97	0.50	0.00	0.00	0.67	0.01	0.37	0.01	0.00	0.00	0.01	0.48	0.09	0.00	0.55	0.01	0.54	0.48
PC	180	0.13	-0.14	0.11	0.476**	-0.379*	-0.19	-0.32	0.22	-0.08	-0.24	0.27	0.466**	-0.08	0.439*	-0.21	0.414*	-0.394*	0.431*	0.421*	-0.389*	0.445*	0.33	0.12	0.427*	0.25	-0.22
S		0.50	0.47	0.58	0.01	0.04	0.31	0.09	0.25	0.67	0.19	0.15	0.01	0.69	0.02	0.27	0.02	0.03	0.02	0.02	0.03	0.01	0.07	0.52	0.02	0.19	0.25
PC	170	0.26	0.26	-0.11	0.418*	0.12	-0.30	0.12	0.438*	0.28	0.14	0.529**	0.34	-0.25	0.521**	0.07	0.409*	-0.34	0.550**	0.466**	-0.13	0.502**	0.448*	.422*	0.532**	0.03	-0.28
S		0.17	0.17	0.56	0.02	0.51	0.11	0.54	0.02	0.14	0.45	0.00	0.06	0.18	0.00	0.72	0.02	0.06	0.00	0.01	0.48	0.00	0.01	0.02	0.00	0.87	0.14
PC	194	0.03	-0.09	0.24	0.24	-0.30	-0.07	-0.09	0.05	-0.18	-0.35	0.451*	0.494**	-0.07	0.397*	-0.04	0.396*	-0.513**	0.436*	0.429*	-0.14	0.26	0.402*	-0.06	0.397*	0.14	-0.12
S		0.88	0.63	0.20	0.21	0.11	0.72	0.64	0.78	0.34	0.06	0.01	0.01	0.71	0.03	0.85	0.03	0.00	0.02	0.02	0.45	0.17	0.03	0.73	0.03	0.45	0.51
PC	total	0.04	-0.10	-0.04	0.511**	-0.29	-0.35	-0.04	0.395*	0.14	-0.05	0.442*	0.508**	-0.08	0.576**	-0.07	0.512**	-0.524**	0.604**	0.544**	-0.379*	0.543**	0.466**	0.19	0.596**	0.07	-0.16
S		0.82	0.61	0.85	0.00	0.12	0.06	0.85	0.03	0.47	0.80	0.01	0.00	0.66	0.00	0.71	0.00	0.00	0.00	0.00	0.04	0.00	0.01	0.32	0.00	0.72	0.41

Table 31: Speke Hall Pearson Product Moment Correlations – Elements versus PCBs

		Si	Al	Ti	Ca	Mg	K	Fe	Mn	S	P	As	Ba	Br	Cd	Cr	Cu	Hg	Ni	Pb	Rb	Sr	V	Y	Zn	Zr	LOI
P	Ace	-0.01	-0.03	0.22	-0.06	-0.16	0.05	-0.17	-0.17	-0.31	-0.28	0.00	0.14	-0.08	-0.06	-0.01	0.12	0.15	-0.01	0.15	0.09	-0.09	0.02	0.15	-0.02	0.365*	-0.12
S		0.95	0.89	0.24	0.74	0.38	0.80	0.37	0.36	0.09	0.12	0.99	0.44	0.66	0.76	0.95	0.51	0.42	0.96	0.43	0.64	0.62	0.91	0.43	0.93	0.04	0.53
P	Flu	-0.13	-0.13	0.03	-0.11	-0.22	0.03	-0.33	-0.19	-0.32	-0.24	-0.24	0.07	-0.01	-0.13	0.04	-0.04	-0.09	-0.09	0.02	0.12	-0.14	-0.10	-0.05	-0.10	0.13	0.04
S		0.48		0.89	0.55	0.23	0.87	0.07	0.30	0.08	0.19	0.20	0.70	0.97	0.48	0.83	0.81	0.63	0.63	0.90	0.53	0.47	0.60	0.79	0.60	0.47	0.84
P	Phe	-0.07	-0.28	0.12	0.00	-0.29	0.01	-0.534**	-0.25	-0.394*	-0.373*	-0.08	0.11	-0.06	-0.05	-0.11	0.13	-0.23	-0.02	0.14	-0.10	0.06	0.03	-0.18	-0.01	0.29	-0.12
S		0.70	0.13	0.51	1.00	0.11	0.95	0.00	0.18	0.03	0.04	0.67	0.57	0.76	0.77	0.55	0.47	0.21	0.92	0.46	0.59	0.76	0.88	0.33	0.96	0.12	0.52
P	Anth	0.09	-0.13	0.23	0.06	-0.380*	0.07	-0.435*	-0.18	-0.427*	-0.476**	0.04	0.32	0.13	0.07	-0.18	0.23	-0.06	0.13	0.16	-0.19	0.02	0.20	-0.11	0.11	0.411*	-0.19
S		0.63	0.47	0.21	0.76	0.04	0.89	0.01	0.34	0.02	0.01	0.83	0.08	0.50	0.71	0.34	0.21	0.75	0.48	0.38	0.30	0.91	0.27	0.56	0.55	0.02	0.30
P	Fluranth	-0.10	-0.30	0.11	0.01	-0.369*	0.04	-0.471**	-0.26	-0.388*	-0.373*	-0.06	0.12	0.05	-0.06	-0.17	0.15	-0.28	-0.04	0.12	-0.08	0.00	0.06	-0.23	-0.02	0.28	-0.12
S		0.58	0.10	0.55	0.97	0.04	0.83	0.01	0.16	0.03	0.04	0.75	0.53	0.77	0.73	0.36	0.43	0.13	0.85	0.52	0.68	1.00	0.75	0.21	0.92	0.13	0.52
P	Pyr	-0.08	-0.393*	0.11	0.04	-0.424*	0.00	-0.544**	-0.24	-0.389*	-0.401*	-0.13	0.10	0.03	-0.06	-0.19	0.12	-0.26	-0.05	0.09	-0.12	0.05	-0.01	-0.23	-0.02	0.28	-0.11
S		0.68	0.03	0.56	0.85	0.02	1.00	0.00	0.19	0.03	0.03	0.48	0.59	0.87	0.75	0.31	0.53	0.16	0.79	0.62	0.50	0.79	0.97	0.21	0.90	0.13	0.56
P	Chry	0.11	-0.18	0.19	0.14	-0.28	0.02	-0.435*	-0.17	-0.360*	-0.422*	0.15	0.27	-0.03	0.07	-0.11	0.27	-0.28	0.11	0.23	-0.09	0.11	0.22	-0.04	0.13	0.431*	-0.26
S		0.56	0.35	0.29	0.44	0.13	0.90	0.01	0.36	0.05	0.02	0.41	0.15	0.89	0.69	0.56	0.15	0.13	0.55	0.20	0.63	0.57	0.24	0.82	0.50	0.02	0.15
P	Benzanth	0.03	-0.28	0.17	0.18	-0.397*	-0.02	-0.415*	-0.13	-0.356*	-0.438*	0.14	0.29	0.10	0.13	-0.09	0.33	-0.32	0.16	0.28	-0.12	0.14	0.20	-0.08	0.16	0.358*	-0.25
S		0.89	0.13	0.35	0.34	0.03	0.90	0.02	0.49	0.05	0.01	0.47	0.12	0.61	0.50	0.62	0.07	0.08	0.40	0.13	0.53	0.46	0.28	0.66	0.39	0.05	0.17
P	Benzbfluranth	0.04	-0.16	0.29	-0.01	-0.24	0.17	-0.33	-0.27	-0.394*	-0.413*	0.01	0.12	0.04	-0.08	-0.08	0.12	-0.17	-0.05	0.10	0.07	-0.07	0.04	-0.11	-0.05	0.413*	-0.14
S		0.84	0.40	0.11	0.95	0.19	0.36	0.07	0.14	0.03	0.02	0.96	0.54	0.85	0.65	0.67	0.51	0.37	0.78	0.58	0.73	0.69	0.83	0.57	0.79	0.02	0.46
P	Benzkfluranth	0.01	-0.12	0.27	-0.07	-0.20	0.19	-0.28	-0.29	-0.388*	-0.383*	0.00	0.07	0.01	-0.12	-0.04	0.09	-0.16	-0.09	0.09	0.15	-0.12	0.01	-0.12	-0.09	0.358*	-0.11
S		0.98	0.53	0.14	0.71	0.28	0.30	0.12	0.11	0.03	0.03	0.99	0.72	0.98	0.52	0.82	0.64	0.38	0.62	0.62	0.42	0.53	0.94	0.52	0.63	0.05	0.56
P	Benzpyr	0.10	-0.16	0.27	-0.04	-0.24	0.19	-0.397*	-0.30	-0.410*	-0.440*	-0.07	0.08	0.07	-0.12	-0.13	0.04	-0.24	-0.11	0.02	0.06	-0.10	-0.03	-0.17	-0.09	0.408*	-0.12
S		0.58	0.38	0.15	0.85	0.19	0.30	0.03	0.10	0.02	0.01	0.73	0.66	0.72	0.52	0.49	0.81	0.19	0.57	0.92	0.76	0.59	0.88	0.35	0.61	0.02	0.52
P	Indeno123pyr	0.16	-0.16	0.13	-0.05	-0.21	0.17	-0.431*	-0.29	-0.35	-0.384*	-0.18	0.04	0.11	-0.16	-0.14	-0.06	-0.30	-0.17	-0.08	0.04	-0.11	-0.12	-0.22	-0.14	0.32	-0.13
S		0.38	0.38	0.49	0.80	0.26	0.37	0.02	0.11	0.05	0.03	0.34	0.83	0.56	0.40	0.45	0.73	0.10	0.36	0.65	0.84	0.56	0.52	0.24	0.44	0.07	0.48
P	benzghiperyl	0.01	-0.17	0.28	-0.05	-0.26	0.17	-0.25	-0.26	-0.355*	-0.377*	-0.04	0.05	0.05	-0.11	-0.08	0.07	-0.11	-0.09	0.07	0.11	-0.12	-0.03	-0.10	-0.09	0.34	-0.06
S		0.97	0.36	0.13	0.78	0.16	0.37	0.17	0.16	0.05	0.04	0.84	0.78	0.77	0.55	0.67	0.69	0.56	0.62	0.71	0.56	0.51	0.87	0.58	0.64	0.06	0.77
P	dibenzahanth	-0.25	-0.10	0.08	-0.22	-0.08	0.09	-0.11	-0.26	-0.23	-0.16	-0.11	-0.10	-0.03	-0.22	-0.06	0.00	0.07	-0.19	0.02	0.24	-0.23	-0.17	-0.10	-0.19	0.21	0.13
S		0.17	0.58	0.68	0.24	0.68	0.62	0.54	0.16	0.21	0.40	0.56	0.58	0.89	0.22	0.75	0.99	0.70	0.30	0.90	0.20	0.22	0.35	0.59	0.31	0.27	0.50
P	totalpah	0.03	-0.20	0.24	-0.01	-0.28	0.14	-0.387*	-0.28	-0.402*	-0.426*	-0.02	0.12	0.05	-0.08	-0.11	0.11	-0.22	-0.06	0.09	0.04	-0.06	0.02	-0.14	-0.05	0.387*	-0.14
S		0.85	0.29	0.19	0.96	0.13	0.46	0.03	0.13	0.02	0.02	0.90	0.54	0.77	0.66	0.57	0.54	0.23	0.75	0.61	0.82	0.74	0.91	0.44	0.79	0.03	0.47
P	TOC	-0.23	-0.14	0.21	**-0.739****	0.13	0.576**	-0.30	**-0.713****	-0.457**	-0.20	**-0.790****	**-0.757****	0.06	**-0.799****	-0.18	**-0.756****	0.01	**-0.830****	-0.651**	0.522**	**-0.757****	-0.699**	-0.656**	**-0.837****	-0.05	0.603**
S		0.22	0.46	0.26	**0.00**	0.50	0.00	0.10	**0.00**	0.01	0.27	**0.00**	**0.00**	0.76	**0.00**	0.35	**0.00**	0.94	**0.00**	0.00	0.00	**0.00**	0.00	0.00	**0.00**	0.77	0.00

Table 32: Speke Hall Pearson Product Moment Correlations – Elements versus PAHs

		PCB18	PCB28	PCB52	PCB49	PCB47	PCB44	PCB66	PCB101	PCB151	PCB118	PCB153	PCB105	PCB141	PCB138	PCB183	PCB128	PCB156	PCB180	PCB170	PCB194	TOTALPCB
P C	1 8	1.00	0.887**	0.804**	0.666**	0.341*	0.637**	0.408*	0.742**	0.646**	0.520**	0.575**	0.411*	0.447**	0.564**	0.714**	0.630**	0.520**	0.572**	0.517**	0.513**	0.805**
S			0.00	0.00	0.00	0.05	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P C	2 8	0.887**	1.00	0.796**	0.719**	0.347*	0.606**	0.475**	0.747**	0.711**	0.701**	0.605**	0.501**	0.567**	0.684**	0.751**	0.721**	0.566**	0.638**	0.396*	0.696**	0.855**
S		0.00		0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
P C	5 2	0.804**	0.796**	1.00	0.695**	0.04	0.30	0.31	0.456**	0.441**	0.487**	0.566**	0.367*	0.32	0.614**	0.426*	0.453**	0.32	0.458**	0.07	0.586**	0.613**
S		0.00	0.00		0.00	0.83	0.09	0.07	0.01	0.01	0.00	0.00	0.03	0.06	0.00	0.01	0.01	0.07	0.01	0.71	0.00	0.00
PC	4 9	0.666**	0.719**	0.695**	1.00	0.32	0.465**	0.459**	0.564**	0.411*	0.397*	0.427*	0.14	0.19	0.465**	0.491**	0.387*	0.15	0.462**	0.14	0.26	0.593**
S		0.00	0.00	0.00		0.06	0.01	0.01	0.00	0.02	0.02	0.01	0.42	0.29	0.01	0.00	0.02	0.40	0.01	0.44	0.14	0.00
PC	4 7	0.341*	0.347*	0.04	0.32	1.00	0.613**	0.555**	0.586**	0.502**	0.523**	0.390*	0.34	0.463**	0.383*	0.460**	0.652**	0.549**	0.428*	0.457**	0.375*	0.590**
S		0.05	0.04	0.83	0.06		0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.01	0.03	0.01	0.00	0.00	0.01	0.01	0.03	0.00
PC	4 4	0.637**	0.606**	0.30	0.465**	0.613**	1.00	0.30	0.577**	0.517**	0.737**	0.525**	0.432*	0.543**	0.398*	0.544**	0.671**	0.662**	0.345*	0.29	0.597**	0.624**
S		0.00	0.00	0.09	0.01	0.00		0.08	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.05	0.09	0.00	0.00
P C	6 6	0.408*	0.475**	0.31	0.459**	0.555**	0.30	1.00	0.676**	0.647**	0.415*	0.30	0.23	0.400*	0.493**	0.511**	0.529**	0.32	0.585**	0.412*	0.379*	0.670**
S		0.02	0.00	0.07	0.01	0.00	0.08		0.00	0.00	0.01	0.08	0.19	0.02	0.00	0.00	0.00	0.07	0.00	0.02	0.03	0.00
PC	101	0.742**	0.747**	0.456**	0.564**	0.586**	0.577**	0.676**	1.00	0.916**	0.661**	0.613**	0.558**	0.676**	0.744**	0.907**	0.848**	0.627**	0.771**	0.663**	0.609**	0.939**
S		0.00	0.00	0.01	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	151	0.646**	0.711**	0.441**	0.411*	0.502**	0.517**	0.647**	0.916**	1.00	0.654**	0.430*	0.596**	0.849**	0.614**	0.895**	0.778**	0.654**	0.693**	0.668**	0.664**	0.880**
S		0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00		0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC	118	0.520**	0.701**	0.487**	0.397*	0.523**	0.737**	0.415*	0.661**	0.654**	1.00	0.658**	0.606**	0.602**	0.689**	0.677**	0.841**	0.730**	0.611**	0.27	0.854**	0.753**
S		0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00
PC	153	0.575**	0.605**	0.566**	.427*	0.390*	0.525**	0.30	0.613**	0.430*	0.658**	1.00	0.617**	0.27	0.797**	0.501**	0.783**	0.646**	0.626**	0.18	0.607**	0.699**
S		0.00	0.00	0.00	0.01	0.02	0.00	0.08	0.00	0.01	0.00		0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.32	0.00	0.00
PC	105	0.411*	0.501**	0.367*	0.14	0.34	0.432*	0.23	0.558**	0.596**	0.606**	0.617**	1.00	0.686**	0.720**	0.567**	0.711**	0.838**	0.627**	0.32	0.759**	0.657**
S		0.02	0.00	0.03	0.42	0.05	0.01	0.19	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00
PC	141	0.447**	0.567**	0.32	0.19	0.463**	0.543**	0.400*	0.676**	0.849**	0.602**	0.27	0.686**	1.00	0.433*	0.714**	0.652**	0.739**	0.434*	0.494**	0.721**	0.675**
S		0.01	0.00	0.06	0.29	0.01	0.00	0.02	0.00	0.00	0.00	0.12	0.00		0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
P C	138	0.564**	0.684**	0.614**	0.465**	0.383*	0.398*	0.493**	0.744**	0.614**	0.689**	0.797**	0.720**	0.433*	1.00	0.697**	0.821**	0.653**	0.843**	0.29	0.730**	0.817**
S		0.00	0.00	0.00	0.01	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01		0.00	0.00	0.00	0.00	0.10	0.00	0.00
PC	183	0.714**	0.751**	0.426*	0.491**	0.460**	0.544**	0.511**	0.907**	0.895**	0.677**	0.501**	0.567**	0.714**	0.697**	1.00	0.798**	0.687**	0.746**	0.618**	0.649**	0.873**
S		0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00
P C	128	0.630**	0.721**	0.453**	0.387*	0.652**	0.671**	0.529**	0.848**	0.778**	0.841**	0.783**	0.711**	0.652**	0.821**	0.798**	1.00	0.805**	0.773**	0.510**	0.796**	0.897**
S		0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PC	156	0.520**	0.566**	0.32	0.15	0.549**	0.662**	0.32	0.627**	0.654**	0.730**	0.646**	0.838**	0.739**	0.653**	0.687**	0.805**	1.00	0.513**	0.463**	0.839**	0.734**
S		0.00	0.00	0.07	0.40	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.01	0.00	0.00
PC	180	0.572**	0.638**	0.458**	.462**	0.428*	0.345*	0.585**	0.771**	0.693**	0.611**	0.626**	0.627**	0.434*	0.843**	0.746**	0.773**	0.513**	1.00	0.400*	0.572**	0.806**
S		0.00	0.00	0.01	0.01	0.01	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00		0.02	0.00	0.00
P C	170	0.517**	0.396*	0.07	0.14	0.457**	0.29	0.412*	0.663**	0.668**	0.27	0.18	0.32	0.494**	0.29	0.618**	0.510**	0.463**	0.400*	1.00	0.347*	0.666**
S		0.00	0.02	0.71	0.44	0.01	0.09	0.02	0.00	0.00	0.12	0.32	0.06	0.00	0.10	0.00	0.00	0.01	0.02		0.04	0.00
PC	194	0.513**	0.696**	0.586**	0.26	0.375*	0.597**	0.379*	0.609**	0.664**	0.854**	0.607**	0.759**	0.721**	0.730**	0.649**	0.796**	0.839**	0.572**	0.347*	1.00	0.760**
S		0.00	0.00	0.00	0.14	0.03	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04		0.00
PC	total	0.805**	0.855**	0.613**	0.593**	0.590**	0.624**	0.670**	0.939**	0.880**	0.753**	0.699**	0.657**	0.675**	0.817**	0.873**	0.897**	0.734**	0.806**	0.666**	0.760**	1.00
S		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

Table 33: Speke Hall Pearson Product Moment Correlations – PCBs versus PCBs

		PCB 18	PCB 28	PCB 52	PCB 49	PCB 47	PCB 44	PCB 66	PCB 101	PCB 151	PCB 118	PCB 153	PCB 105	PCB 141	PCB 138	PCB 183	PCB 128	PCB 156	PCB 180	PCB 170	PC B194	TOTAL PCB
P C	KAPPA	-0.23	-0.04	-0.15	-0.31	0.15	0.01	0.22	0.17	0.29	0.358*	0.05	0.390*	0.32	0.25	0.24	0.377*	0.352*	0.29	0.13	0.435*	0.17
S		0.19	0.82	0.39	0.08	0.41	0.96	0.21	0.34	0.10	0.04	0.77	0.02	0.06	0.16	0.17	0.03	0.04	0.10	0.45	0.01	0.33
P C	χ L F	-0.23	-0.04	-0.15	-0.29	0.17	0.01	0.24	0.18	0.29	0.365*	0.06	0.387*	0.32	0.26	0.25	0.389*	0.353*	0.30	0.13	0.433*	0.18
S		0.19	0.84	0.38	0.10	0.33	0.93	0.18	0.30	0.09	0.03	0.72	0.02	0.07	0.13	0.15	0.02	0.04	0.09	0.45	0.01	0.31
P C	FD%	-0.10	-0.11	-0.23	0.15	0.360*	0.06	0.20	0.18	-0.01	-0.01	0.07	-0.08	-0.11	0.14	0.06	0.08	-0.05	0.06	0.00	-0.14	0.04
S		0.58	0.52	0.20	0.39	0.04	0.75	0.26	0.31	0.97	0.95	0.68	0.67	0.55	0.43	0.73	0.63	0.80	0.73	0.99	0.44	0.83
PC	SIRM	-0.400*	-0.25	-0.32	-0.407*	0.06	-0.13	0.05	-0.07	0.03	0.16	-0.06	0.27	0.11	0.06	0.02	0.17	0.21	0.10	0.01	0.23	-0.05
S		0.02	0.16	0.06	0.02	0.76	0.46	0.79	0.70	0.87	0.37	0.75	0.13	0.54	0.74	0.91	0.33	0.23	0.57	0.95	0.19	0.76
PC	χARM	-0.541**	-0.536**	-0.503**	-0.524**	-0.28	-0.405*	-0.360*	-0.528**	-0.492**	-0.30	-0.31	-0.11	-0.345*	-0.395*	-0.465**	-0.33	-0.21	-0.370*	-0.24	-0.24	-0.510**
S		0.00	0.00	0.00	0.00	0.11	0.02	0.04	0.00	0.00	0.09	0.08	0.53	0.05	0.02	0.01	0.06	0.24	0.03	0.18	0.18	0.00
PC	χARM/SIRM	-0.363*	-0.487**	-0.32	-0.28	-0.525**	-0.445**	-0.590**	**-0.737****	**-0.786****	-0.586**	-0.385*	-0.477**	-0.655**	-0.632**	**-0.721****	-0.682**	-0.568**	-0.642**	-0.467**	-0.575**	**-0.711****
S		0.03	0.00	0.07	0.10	0.00	0.01	0.00	**0.00**	**0.00**	0.00	0.02	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00	0.01	0.00	**0.00**
PC	SIRM/χLF	-0.563**	-0.604**	-0.498**	-0.433*	-0.27	-0.429*	-0.436*	-0.629**	-0.618**	-0.433*	-0.32	-0.20	-0.465**	-0.467**	-0.551**	-0.461**	-0.28	-0.426*	-0.30	-0.398*	-0.588**
S		0.00	0.00	0.00	0.01	0.13	0.01	0.01	0.00	0.00	0.01	0.06	0.26	0.01	0.01	0.00	0.01	0.11	0.01	0.09	0.02	0.00
PC	χARM/χLF	-0.435*	-0.552**	-0.409*	-0.357*	-0.476**	-0.476**	-0.576**	**-0.731****	**-0.765****	-0.578**	-0.395*	-0.412*	-0.627**	-0.620**	-0.698**	-0.650**	-0.510**	-0.610**	-0.408*	-0.559**	**-0.705****
S		0.01	0.00	0.02	0.04	0.00	0.00	0.00	**0.00**	**0.00**	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	**0.00**
PC	HIRM	-0.396*	-0.25	-0.32	-0.406*	0.06	-0.13	0.05	-0.06	0.04	0.16	-0.06	0.27	0.11	0.06	0.02	0.18	0.21	0.10	0.02	0.23	-0.05
S		0.02	0.16	0.07	0.02	0.74	0.48	0.76	0.72	0.84	0.36	0.75	0.13	0.52	0.74	0.90	0.32	0.22	0.58	0.92	0.19	0.78
PC	HARD %	0.00	-0.06	0.09	0.11	-0.26	-0.16	-0.31	-0.24	-0.359*	-0.25	0.04	-0.17	-0.366*	-0.06	-0.20	-0.25	-0.28	0.00	-0.364*	-0.27	-0.23
S		0.99	0.75	0.62	0.53	0.13	0.37	0.07	0.17	0.04	0.15	0.84	0.34	0.03	0.72	0.25	0.16	0.11	0.99	0.03	0.13	0.19
PC	A R M	-0.541**	-0.536**	-0.503**	-0.524**	-0.28	-0.405*	-0.360*	-0.528**	-0.492**	-0.30	-0.31	-0.11	-0.345*	-0.395*	-0.465**	-0.33	-0.21	-0.370*	-0.24	-0.24	-0.510**
S		0.00	0.00	0.00	0.00	0.11	0.02	0.04	0.00	0.00	0.09	0.08	0.53	0.05	0.02	0.01	0.06	0.24	0.03	0.18	0.18	0.00
PC	SIRM/ARM	0.390*	0.478**	0.28	0.30	0.558**	.435*	0.590**	**0.798****	**0.841****	0.567**	0.363*	0.481**	0.681**	0.630**	**0.787****	0.692**	0.564**	0.664**	0.552**	0.540**	**0.740****
S		0.02	0.00	0.11	0.08	0.00	0.01	0.00	**0.00**	**0.00**	0.00	0.03	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00	0.00	0.00	**0.00**
P C	Soft	-0.26	-0.06	-0.16	-0.31	0.20	0.01	0.24	0.13	0.25	0.355*	0.04	0.408*	0.30	0.25	0.19	0.364*	0.354*	0.30	0.12	0.438**	0.16
S		0.14	0.76	0.38	0.07	0.27	0.95	0.17	0.47	0.16	0.04	0.84	0.02	0.08	0.15	0.29	0.03	0.04	0.09	0.49	0.01	0.36
PC	-20mT	.434*	0.524**	0.462**	0.31	0.29	0.359*	0.419*	0.467**	0.502**	0.409*	0.22	0.27	0.434*	0.437**	0.395*	0.394*	0.29	0.426*	0.28	0.423*	0.520**
S		0.01	0.00	0.01	0.08	0.09	0.04	0.01	0.01	0.00	0.02	0.21	0.12	0.01	0.01	0.02	0.02	0.09	0.01	0.11	0.01	0.00
P C	-300mT	0.00	0.06	-0.09	-0.11	0.26	0.16	0.31	0.24	0.359*	0.25	-0.04	0.17	0.366*	0.06	0.20	0.25	0.28	0.00	0.364*	0.27	0.23
S		0.99	0.75	0.62	0.53	0.13	0.37	0.07	0.17	0.04	0.15	0.84	0.34	0.03	0.72	0.25	0.16	0.11	0.99	0.03	0.13	0.19
PC	Soft/ARM	0.446**	0.537**	0.345*	0.32	0.542**	0.451**	0.601**	**0.794****	**0.843****	0.576**	0.342*	0.481**	0.693**	0.639**	**0.763****	0.680**	0.547**	0.668**	0.560**	0.563**	**0.758****
S		0.01	0.00	0.05	0.06	0.00	0.01	0.00	**0.00**	**0.00**	0.00	0.05	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00	0.00	0.00	**0.00**
PC	Soft/fd%	0.00	0.01	-0.19	-0.09	0.09	0.11	0.06	0.10	0.07	0.04	-0.03	0.09	0.11	0.03	0.07	0.10	0.03	0.03	0.11	0.04	0.05
S		1.00	0.96	0.31	0.62	0.61	0.54	0.73	0.59	0.69	0.85	0.88	0.63	0.57	0.85	0.70	0.57	0.87	0.88	0.54	0.81	0.80
P C	χARM/FDS	0.00	0.01	-0.19	-0.09	0.09	0.11	0.06	0.10	0.07	0.04	-0.03	0.09	0.11	0.03	0.07	0.10	0.03	0.03	0.11	0.04	0.05
S		1.00	0.96	0.31	0.62	0.61	0.54	0.73	0.59	0.69	0.85	0.88	0.63	0.57	0.85	0.70	0.57	0.87	0.88	0.54	0.81	0.80

Table 34: Speke Hall Pearson Product Moment Correlations – PCBs versus Magnetics

		PCB 18	PCB 28	PCB 52	PCB 49	PCB 47	PCB 44	PCB 66	PCB 101	PCB 151	PCB 118	PCB 153	PCB 105	PCB 141	PCB 138	PCB 183	PCB 128	PCB 156	PCB 180	PCB 170	PC B194	TOTAL PCB
P C	Mean	0.10	0.14	0.29	0.29	-0.422*	-0.18	-0.25	-0.25	-0.24	-0.21	-0.11	-0.10	-0.23	-0.21	-0.21	-0.28	-0.33	-0.12	-0.349*	-0.20	-0.20
S		0.57	0.43	0.09	0.10	0.01	0.31	0.16	0.15	0.18	0.24	0.55	0.58	0.19	0.23	0.24	0.10	0.06	0.50	0.04	0.25	0.26
P C	Sorting	-0.16	-0.357*	-0.362*	-0.24	0.09	-0.13	-0.21	-0.12	-0.22	-0.19	0.00	-0.19	-0.24	-0.08	-0.05	-0.12	0.02	-0.15	0.12	-0.22	-0.15
S		0.38	0.04	0.04	0.17	0.63	0.46	0.23	0.52	0.20	0.28	1.00	0.29	0.17	0.67	0.77	0.50	0.92	0.41	0.51	0.21	0.38
P C	Skewness	-0.27	-0.25	-0.16	-0.16	-0.09	-0.16	-0.01	-0.11	-0.14	0.00	-0.03	0.02	-0.12	0.02	-0.10	-0.05	-0.01	-0.05	-0.07	0.06	-0.11
S		0.13	0.15	0.38	0.36	0.59	0.37	0.93	0.52	0.42	1.00	0.89	0.91	0.50	0.89	0.59	0.77	0.98	0.76	0.69	0.74	0.52
PC	Kurtosis	0.12	0.25	0.30	0.24	-0.21	0.14	-0.08	-0.04	-0.04	0.24	0.08	0.15	-0.02	0.12	0.03	0.04	0.01	0.09	-0.18	0.23	0.06
S		0.48	0.16	0.08	0.17	0.22	0.44	0.67	0.82	0.81	0.16	0.63	0.40	0.93	0.49	0.88	0.81	0.93	0.61	0.31	0.20	0.73
PC	%Sand	0.09	0.18	0.29	0.27	-0.388*	-0.11	-0.14	-0.17	-0.13	-0.11	-0.09	-0.03	-0.11	-0.17	-0.15	-0.19	-0.28	-0.06	-0.31	-0.11	-0.13
S		0.59	0.31	0.10	0.12	0.02	0.52	0.42	0.35	0.47	0.53	0.59	0.88	0.53	0.33	0.41	0.29	0.11	0.72	0.07	0.54	0.46
PC	%Mud	-0.09	-0.18	-0.29	-0.27	0.388*	0.11	0.14	0.17	0.13	0.11	0.09	0.03	0.11	0.17	0.15	0.19	0.28	0.06	0.31	0.11	0.13
S		0.59	0.31	0.10	0.12	0.02	0.52	0.42	0.35	0.47	0.53	0.59	0.88	0.53	0.33	0.41	0.29	0.11	0.72	0.07	0.54	0.46
PC	%coarse sand	-0.08	-0.07	-0.04	0.10	-0.06	-0.15	-0.03	0.03	-0.02	0.00	0.02	0.07	-0.04	0.03	0.07	0.02	-0.05	0.08	-0.01	-0.05	-0.01
S		0.67	0.71	0.83	0.59	0.72	0.41	0.89	0.88	0.92	1.00	0.90	0.69	0.80	0.88	0.71	0.90	0.78	0.65	0.97	0.79	0.97
PC	%coars sand	-0.10	-0.10	0.09	0.04	-0.484**	-0.31	-0.385*	-0.405*	-0.417*	-0.24	-0.16	-0.19	-0.398*	-0.26	-0.30	-0.372*	-0.341*	-0.24	-0.379*	-0.24	-0.347*
S		0.58	0.56	0.61	0.80	0.00	0.08	0.02	0.02	0.01	0.17	0.37	0.27	0.02	0.14	0.08	0.03	0.05	0.18	0.03	0.18	0.04
PC	%medium sand	0.10	0.07	0.24	0.28	-0.430*	-0.22	-0.353*	-0.33	-0.346*	-0.347*	-0.13	-0.21	-0.34	-0.30	-0.28	-0.391*	-0.393*	-0.22	-0.381*	-0.351*	-0.29
S		0.57	0.69	0.17	0.12	0.01	0.21	0.04	0.06	0.05	0.04	0.46	0.23	0.05	0.08	0.11	0.02	0.02	0.22	0.03	0.04	0.10
PC	%fine sand	0.16	0.32	0.29	0.23	-0.21	0.06	0.09	0.08	0.18	0.12	-0.04	0.17	0.18	0.00	0.07	0.08	-0.09	0.14	-0.11	0.12	0.10
S		0.37	0.07	0.09	0.18	0.23	0.74	0.60	0.64	0.31	0.49	0.83	0.35	0.30	0.98	0.68	0.67	0.63	0.43	0.52	0.49	0.59
PC	%vfine sand	-0.10	-0.07	-0.21	-0.25	0.434*	0.25	0.362*	0.30	0.31	0.32	0.14	0.17	0.32	0.27	0.22	0.356*	0.370*	0.16	0.33	0.34	0.26
S		0.59	0.71	0.23	0.16	0.01	0.15	0.04	0.08	0.07	0.06	0.44	0.33	0.06	0.12	0.21	0.04	0.03	0.36	0.05	0.05	0.13
PC	% vcoarse silt	-0.11	-0.15	-0.27	-0.28	0.421*	0.14	0.23	0.22	0.20	0.19	0.11	0.09	0.19	0.23	0.19	0.26	0.33	0.12	0.33	0.20	0.19
S		0.55	0.40	0.12	0.11	0.01	0.43	0.18	0.21	0.25	0.29	0.53	0.62	0.28	0.20	0.28	0.14	0.06	0.51	0.06	0.25	0.29
P C	%coarse silt	-0.16	-0.28	-0.371*	-0.33	0.33	0.03	0.04	0.06	0.02	0.00	0.02	-0.04	0.02	0.07	0.06	0.09	0.20	-0.03	0.27	-0.01	0.02
S		0.36	0.11	0.03	0.06	0.06	0.86	0.84	0.72	0.90	0.99	0.89	0.81	0.91	0.71	0.73	0.62	0.26	0.87	0.13	0.96	0.90
PC	%medium silt	-0.04	-0.16	-0.27	-0.19	0.378*	0.12	0.08	0.12	0.07	0.03	0.06	-0.06	0.04	0.10	0.13	0.11	0.22	0.02	0.30	0.00	0.10
S		0.84	0.36	0.13	0.28	0.03	0.48	0.67	0.49	0.71	0.86	0.72	0.74	0.84	0.56	0.48	0.54	0.22	0.93	0.08	0.99	0.58
P C	%fine silt	0.02	-0.09	-0.18	-0.14	0.361*	0.14	0.06	0.13	0.06	0.06	0.13	-0.02	0.04	0.16	0.11	0.13	0.23	0.04	0.28	0.04	0.13
S		0.90	0.61	0.32	0.41	0.04	0.42	0.72	0.45	0.73	0.73	0.47	0.92	0.84	0.35	0.55	0.48	0.20	0.81	0.11	0.83	0.46
PC	%vfine silt	-0.03	-0.16	-0.27	-0.18	0.33	0.16	-0.02	0.08	-0.01	0.05	0.13	-0.03	-0.02	0.13	0.10	0.11	0.23	0.00	0.19	-0.01	0.06
S		0.88	0.37	0.12	0.32	0.06	0.38	0.92	0.65	0.94	0.77	0.48	0.87	0.93	0.47	0.58	0.55	0.19	0.98	0.28	0.94	0.75
PC	%clay	0.00	-0.13	-0.27	-0.17	0.363*	0.15	0.11	0.15	0.10	0.05	0.04	-0.05	0.09	0.11	0.15	0.10	0.22	0.01	0.29	0.02	0.11
		0.98	0.47	0.13	0.33	0.03	0.39	0.52	0.38	0.57	0.80	0.83	0.77	0.63	0.53	0.39	0.59	0.22	0.95	0.09	0.89	0.53

Table 35: Speke Hall Pearson Product Moment Correlations – PCBs versus Grain Size

		PCB 18	PCB 28	PCB 52	PCB 49	PCB 47	PCB 44	PCB 66	PCB 101	PCB 151	PCB 118	PCB 153	PCB 105	PCB 141	PCB 138	PCB 183	PCB 128	PCB 156	PCB 180	PCB 170	PC B194	TOTAL PCB
P C	Acy	-0.21	-0.20	-0.28	-0.16	-0.03	-0.21	0.10	0.10	0.07	-0.01	0.08	0.19	-0.07	0.17	0.11	0.16	-0.01	0.28	0.01	-0.07	0.00
S		0.22	0.26	0.11	0.32	0.88	0.23	0.56	0.58	0.68	0.97	0.65	0.29	0.68	0.34	0.54	0.36	0.97	0.11	0.97	0.70	0.99
P C	Flu	0.07	0.10	0.06	0.20	0.09	0.05	0.14	0.17	0.03	0.10	0.33	0.25	-0.08	0.30	-0.03	0.23	-0.07	0.33	-0.22	0.00	0.11
S		0.71	0.57	0.74	0.25	0.61	0.78	0.44	0.34	0.89	0.56	0.06	0.16	0.67	0.08	0.86	0.19	0.71	0.06	0.21	0.99	0.55
P C	Phe	0.00	0.06	0.09	0.06	0.02	0.02	0.33	0.25	0.16	0.16	0.27	0.23	-0.04	0.381*	0.10	0.33	-0.01	0.407*	-0.01	0.13	0.21
S		0.99	0.72	0.63	0.73	0.93	0.93	0.06	0.15	0.37	0.37	0.13	0.18	0.84	0.03	0.57	0.05	0.97	0.02	0.94	0.48	0.24
PC	Anth	-0.10	0.01	-0.04	-0.06	0.06	-0.11	0.27	0.27	0.21	0.17	0.22	0.26	0.05	0.389*	0.18	0.379*	0.03	0.434*	0.02	0.13	0.19
S		0.59	0.96	0.82	0.73	0.72	0.52	0.13	0.12	0.24	0.34	0.20	0.14	0.78	0.02	0.30	0.03	0.88	0.01	0.91	0.46	0.29
PC	Fluoranth	-0.01	0.05	0.06	0.06	0.02	0.00	0.25	0.24	0.17	0.16	0.22	0.22	0.01	0.374*	0.19	0.344*	0.04	0.412*	-0.01	0.13	0.19
S		0.95	0.77	0.72	0.72	0.89	1.00	0.16	0.16	0.34	0.38	0.21	0.21	0.96	0.03	0.27	0.05	0.82	0.02	0.96	0.45	0.27
PC	Pyr	0.02	0.06	0.07	0.07	-0.04	0.00	0.29	0.25	0.15	0.13	0.23	0.15	-0.05	0.366*	0.19	0.30	-0.01	0.416*	-0.04	0.10	0.18
S		0.92	0.74	0.68	0.69	0.83	0.99	0.09	0.16	0.38	0.45	0.19	0.39	0.76	0.03	0.29	0.08	0.95	0.01	0.80	0.58	0.30
PC	Chry	0.03	0.11	0.06	0.10	0.14	0.00	0.28	0.32	0.29	0.20	0.19	0.354*	0.14	0.409*	0.33	0.384*	0.17	0.472**	0.10	0.20	0.27
S		0.88	0.55	0.75	0.58	0.45	0.98	0.11	0.07	0.09	0.26	0.28	0.04	0.42	0.02	0.05	0.03	0.33	0.00	0.58	0.25	0.12
PC	benzant	0.07	0.15	0.08	0.11	0.15	0.02	0.356*	0.387*	0.360*	0.26	0.26	0.386*	0.18	0.476**	0.422*	0.443**	0.24	0.564**	0.14	0.26	0.348*
S		0.69	0.39	0.63	0.52	0.40	0.89	0.04	0.02	0.04	0.14	0.14	0.02	0.30	0.00	0.01	0.01	0.17	0.00	0.42	0.13	0.04
PC	benzbee	-0.09	-0.01	-0.04	0.02	-0.03	-0.14	0.12	0.17	0.15	0.08	0.13	0.26	0.04	0.29	0.29	0.24	0.11	0.382*	-0.01	0.09	0.12
S		0.60	0.97	0.83	0.91	0.88	0.44	0.49	0.34	0.40	0.65	0.46	0.14	0.84	0.09	0.09	0.17	0.52	0.03	0.96	0.62	0.50
PC	benzfluor	-0.10	-0.03	-0.05	0.01	-0.05	-0.14	0.08	0.12	0.10	0.06	0.11	0.25	0.01	0.26	0.24	0.21	0.11	0.33	0.00	0.08	0.09
S		0.57	0.87	0.77	0.96	0.80	0.44	0.67	0.51	0.57	0.75	0.53	0.15	0.96	0.14	0.17	0.23	0.54	0.06	0.98	0.65	0.59
PC	benzper	-0.02	0.04	0.01	0.04	-0.04	-0.09	0.14	0.20	0.16	0.11	0.17	0.27	0.04	0.31	0.29	0.26	0.12	0.405*	0.00	0.13	0.16
S		0.92	0.84	0.94	0.82	0.83	0.61	0.45	0.26	0.37	0.53	0.34	0.12	0.83	0.07	0.09	0.14	0.50	0.02	1.00	0.45	0.38
PC	benzPyr	0.07	0.07	0.06	0.12	-0.03	-0.04	0.15	0.22	0.15	0.11	0.19	0.28	0.02	0.31	0.25	0.21	0.08	0.398*	-0.02	0.13	0.17
S		0.70	0.71	0.73	0.48	0.85	0.81	0.40	0.21	0.41	0.54	0.29	0.12	0.91	0.08	0.16	0.22	0.64	0.02	0.93	0.48	0.34
P C	indpyr	-0.08	-0.01	-0.04	0.03	-0.08	-0.13	0.08	0.11	0.10	0.05	0.10	0.18	0.00	0.24	0.27	0.18	0.08	0.32	-0.06	0.06	0.07
S		0.64	0.94	0.84	0.88	0.85	0.45	0.64	0.55	0.58	0.79	0.57	0.31	1.00	0.18	0.13	0.32	0.65	0.06	0.74	0.73	0.69
PC	dibenzahan	-0.20	-0.14	-0.10	-0.03	-0.17	-0.24	-0.01	-0.10	-0.09	-0.12	0.01	0.09	-0.15	0.04	-0.06	-0.02	-0.11	0.10	-0.13	-0.15	-0.10
S		0.26	0.42	0.59	0.87	0.33	0.18	0.95	0.59	0.62	0.48	0.94	0.60	0.39	0.81	0.74	0.92	0.52	0.58	0.48	0.41	0.58
P C	totalpah	-0.04	0.02	0.00	0.05	-0.02	-0.10	0.17	0.20	0.17	0.11	0.16	0.27	0.03	0.33	0.28	0.27	0.10	0.411*	0.00	0.11	0.16
S		0.81	0.90	1.00	0.78	0.92	0.59	0.35	0.25	0.35	0.55	0.35	0.12	0.85	0.06	0.10	0.13	0.56	0.02	0.99	0.52	0.38
PC	TOC	-0.13	-0.16	-0.05	-0.15	-0.412*	-0.18	-0.385*	-0.435*	-0.560**	-0.14	0.04	-0.30	-0.491**	-0.16	-0.439**	-0.28	-0.34	-0.25	-0.574**	-0.23	-0.408*
S		0.45	0.38	0.76	0.40	0.02	0.30	0.02	0.01	0.00	0.42	0.81	0.09	0.00	0.37	0.01	0.11	0.05	0.16	0.00	0.20	0.02

Table 36: Speke Hall Pearson Product Moment Correlations – PCBs versus PAHs

		Ace	Flu	Phenanth	Anth	Fluoranth	Pyr	Chry	Benzanthr	Benzbfluanth	Benzkfluranth	Benzapyr	Indeno123cdpyr	benzghiperyl	dibenzahanthr	totalpah	TOC
P C	A c e	1.00	0.552**	0.515**	0.504**	0.518**	0.522**	0.563**	0.591**	0.665**	0.673**	0.605**	0.497**	0.668**	0.684**	0.651**	-0.04
S			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.83
P C	F l u	0.552**	1.00	0.624**	0.481**	0.459**	0.490**	0.352*	0.348*	0.27	0.26	0.29	0.371*	0.22	0.380*	0.336*	0.21
S		0.00		0.00	0.00	0.01	0.00	0.04	0.04	0.12	0.13	0.10	0.03	0.21	0.02	0.05	0.22
P C	P h e	0.515**	0.624**	1.00	**0.766****	**0.890****	**0.920****	**0.738****	**0.727****	0.568**	0.544**	0.605**	0.589**	0.455**	0.449**	0.658**	0.04
S		0.00	0.00		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.82
PC	A n t h r	0.504**	00.481**	**0.766****	1.00	**0.760****	**0.728****	**0.723****	**0.717****	0.591**	0.530**	0.579**	0.482**	0.469**	0.378*	0.624**	-0.08
S		0.00	0.00	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.66
PC	Fluoranth	0.518**	.459**	**0.890****	**0.760****	1.00	**0.964****	**0.907****	**0.885****	**0.795****	**0.778****	**0.834****	**0.784****	**0.708****	0.586**	**0.868****	0.06
S		0.00	0.01	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.00	**0.00**	0.74
PC	P y r	0.522**	0.490**	**0.920****	**0.728****	**0.964****	1.00	**0.842****	**0.844****	**0.743****	**0.712****	**0.800****	**0.774****	0.674**	0.528**	**0.826****	0.08
S		0.00	0.00	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.00	0.00	**0.00**	0.65
PC	C h r y	0.563**	0.352*	**0.738****	**0.723****	**0.907****	**0.842****	1.00	**0.951****	**0.892****	**0.867****	**0.906****	**0.828****	**0.806****	0.618**	**0.931****	-0.13
S		0.00	0.04	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.00	**0.00**	0.47
PC	Benzanthr	0.591**	0.348*	**0.727****	**0.717****	**0.885****	**0.844****	**0.951****	1.00	**0.911****	**0.883****	**0.916****	**0.831****	**0.839****	0.626**	**0.943****	-0.15
S		0.00	0.04	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.00	**0.00**	0.38
PC	Benzbfluanth	0.665**	0.27	0.568**	0.591**	**0.795****	**0.743****	**0.892****	**0.911****	1.00	**0.987****	**0.968****	**0.833****	**0.972****	**0.782****	**0.984****	-0.02
S		0.00	0.12	0.00	0.00	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.93
PC	Benzkfluranth	0.673**	0.26	0.544**	0.530**	**0.778****	**0.712****	**0.867****	**0.883****	**0.987****	1.00	**0.951****	**0.818****	**0.974****	**0.829****	**0.973****	0.00
S		0.00	0.13	0.00	0.00	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.98
PC	B e n z a p y r	0.605**	0.29	0.605**	0.579**	**0.834****	**0.800****	**0.906****	**0.916****	**0.968****	**0.951****	1.00	**0.934****	**0.942****	**0.703****	**0.988****	0.03
S		0.00	0.10	0.00	0.00	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**	**0.00**	0.88
PC	Indeno123cdpyr	0.497**	0.371*	0.589**	0.482**	**0.784****	**0.774****	**0.828****	**0.831****	**0.833****	**0.818****	0.934**	1.00	**0.807****	0.566**	**0.898****	0.07
S		0.00	0.03	0.00	0.00	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.00		**0.00**	0.00	**0.00**	0.68
P C	benzghiperyl	0.668**	0.22	0.455**	0.469**	**0.708****	0.674**	**0.806****	**0.839****	**0.972****	**0.974****	0.942**	**0.807****	1.00	**0.804****	**0.951****	0.03
S		0.00	0.21	0.01	0.00	**0.00**	0.00	**0.00**	**0.00**	**0.00**	**0.00**	0.00	**0.00**		**0.00**	**0.00**	0.87
PC	dibenzahanth	0.684**	0.380*	0.449**	0.378*	0.586**	0.528**	0.618**	0.626**	**0.782****	**0.829****	0.703**	0.566**	**0.804****	1.00	**0.759****	0.12
S		0.00	0.02	0.01	0.03	0.00	0.00	0.00	0.00	**0.00**	**0.00**	0.00	0.00	**0.00**		**0.00**	0.51
P C	t o t a l p a h	0.651**	0.336*	0.658**	0.624**	**0.868****	**0.826****	**0.931****	**0.943****	**0.984****	**0.973****	**0.988****	**0.898****	**0.951****	**0.759****	1.00	0.00
S		0.00	0.05	0.00	0.00	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		0.99
PC	T O C	-0.04	0.21	0.04	-0.08	0.06	0.08	-0.13	-0.15	-0.02	0.00	0.03	0.07	0.03	0.12	0.00	1.00
S		0.83	0.22	0.82	0.66	0.74	0.65	0.47	0.38	0.93	0.98	0.88	0.68	0.87	0.51	0.99	

Table 37: Speke Hall Pearson Product Moment Correlations – PAHs versus PAHs

		Ace	Flu	Phe	Anth	Fluoranth	Pyr	Chry	Benzanthr	Benzbfluoranth	Benzkfluoranth	Benzapyr	Indeno123cdpy	benzghipery	dibenzahanth	Total pah	TOC
P C	K A P P A	0.459**	0.13	0.406*	0.530**	0.452**	0.377*	0.547**	0.530**	0.479**	0.471**	0.441**	0.32	0.418*	0.22	0.472**	-0.11
S		0.01	0.45	0.02	0.00	0.01	0.03	0.00	0.00	0.00	0.00	0.01	0.06	0.01	0.20	0.00	0.54
P C	χ L F	0.470**	0.14	0.406*	0.536**	0.451**	0.375*	0.550**	0.530**	0.483**	0.473**	0.440**	0.31	0.420*	0.22	0.473**	-0.11
S		0.00	0.41	0.02	0.00	0.01	0.03	0.00	0.00	0.00	0.00	0.01	0.07	0.01	0.20	0.00	0.52
P C	F D %	0.337*	0.25	0.02	0.13	0.00	-0.01	0.10	0.03	0.10	0.08	0.05	0.02	0.11	0.13	0.07	-0.09
S		0.05	0.14	0.93	0.45	1.00	0.95	0.55	0.87	0.56	0.65	0.77	0.93	0.52	0.46	0.67	0.61
PC	S I R M	0.539**	0.13	0.30	0.419*	0.357*	0.28	0.455**	0.407*	0.465**	0.484**	0.410*	0.28	0.433**	0.30	0.438**	-0.02
S		0.00	0.46	0.08	0.01	0.04	0.11	0.01	0.02	0.00	0.00	0.01	0.10	0.01	0.08	0.01	0.93
PC	χ A R M	0.392*	0.12	0.06	0.15	0.11	0.06	0.15	0.07	0.23	0.28	0.23	0.20	0.25	0.28	0.22	0.337*
S		0.02	0.48	0.74	0.41	0.51	0.75	0.39	0.70	0.18	0.10	0.19	0.24	0.15	0.11	0.21	0.05
PC	χ A R M / S I R M	-0.04	0.05	-0.19	-0.22	-0.16	-0.15	-0.23	-0.30	-0.10	-0.06	-0.05	0.04	-0.05	0.12	-0.10	0.616**
S		0.83	0.76	0.29	0.20	0.37	0.38	0.19	0.08	0.55	0.75	0.76	0.82	0.78	0.50	0.57	0.00
PC	S I R M / χ L F	0.346*	0.01	-0.15	-0.12	-0.10	-0.14	-0.07	-0.15	0.11	0.19	0.08	0.06	0.18	0.27	0.07	0.21
S		0.04	0.97	0.39	0.48	0.56	0.44	0.70	0.38	0.52	0.28	0.65	0.74	0.31	0.12	0.70	0.23
PC	χ A R M / χ L F	0.10	0.05	-0.19	-0.20	-0.14	-0.15	-0.18	-0.26	-0.04	0.02	0.00	0.07	0.02	0.18	-0.04	0.525**
S		0.57	0.78	0.29	0.25	0.42	0.38	0.30	0.13	0.84	0.89	1.00	0.68	0.89	0.30	0.81	0.00
PC	H I R M	0.535**	0.13	0.30	0.415*	0.353*	0.27	0.451**	0.401*	0.455**	0.475**	0.401*	0.28	0.424*	0.30	0.429*	-0.02
S		0.00	0.47	0.08	0.01	0.04	0.11	0.01	0.02	0.01	0.00	0.02	0.11	0.01	0.09	0.01	0.89
PC	H A R D %	-0.17	0.10	-0.02	-0.08	0.04	0.09	-0.05	0.01	0.13	0.10	0.15	0.17	0.13	0.16	0.11	0.433**
S		0.33	0.56	0.89	0.66	0.83	0.61	0.77	0.95	0.45	0.56	0.40	0.32	0.45	0.37	0.53	0.01
PC	A R M	0.392*	0.12	0.06	0.14	0.11	0.05	0.15	0.07	0.23	0.28	0.23	0.20	0.25	0.28	0.22	.337*
S		0.02	0.48	0.74	0.41	0.51	0.75	0.39	0.70	0.18	0.10	0.19	0.24	0.15	0.11	0.21	0.05
PC	S I R M / A R M	0.10	-0.05	0.16	0.24	0.16	0.15	0.27	0.33	0.14	0.09	0.09	0.02	0.09	-0.11	0.13	-0.692**
S		0.57	0.78	0.37	0.17	0.37	0.38	0.12	0.05	0.43	0.62	0.60	0.93	0.62	0.54	0.45	0.00
P C	S o f t	0.426*	0.12	0.400*	0.520**	0.427*	0.342*	0.516**	0.505**	0.442**	0.439**	0.392*	0.27	0.365*	0.20	0.430**	-0.13
S		0.01	0.49	0.02	0.00	0.01	0.04	0.00	0.00	0.01	0.01	0.02	0.12	0.03	0.25	0.01	0.44
PC	- 2 0 m T	-0.433**	-0.12	0.10	0.08	0.01	0.02	-0.03	0.07	-0.22	-0.27	-0.21	-0.19	-0.31	-0.347*	-0.19	-0.31
S		0.01	0.50	0.56	0.65	0.94	0.89	0.84	0.69	0.21	0.11	0.23	0.27	0.07	0.04	0.28	0.07
P C	- 3 0 0 m T	0.17	-0.10	0.02	0.08	-0.04	-0.09	0.05	-0.01	-0.13	-0.10	-0.15	-0.17	-0.13	-0.16	-0.11	-0.433**
S		0.33	0.56	0.89	0.66	0.83	0.61	0.77	0.95	0.45	0.56	0.40	0.32	0.45	0.37	0.53	0.01
PC	S o f t / A R M	-0.02	-0.07	0.16	0.22	0.13	0.13	0.21	0.29	0.05	0.00	0.02	-0.03	-0.02	-0.19	0.06	-0.668**
S		0.90	0.70	0.36	0.21	0.45	0.45	0.22	0.09	0.78	0.98	0.92	0.85	0.90	0.28	0.75	0.00
PC	S o f t / f d %	0.23	0.21	0.22	0.26	0.24	0.22	0.22	0.21	0.22	0.21	0.22	0.21	0.19	0.19	0.23	-0.26
S		0.20	0.24	0.22	0.14	0.19	0.23	0.21	0.23	0.22	0.23	0.22	0.24	0.28	0.30	0.20	0.14
P C	χ A R M / F D %	0.23	0.21	0.22	0.26	0.24	0.22	0.22	0.21	0.22	0.21	0.22	0.21	0.19	0.19	0.23	-0.26
S		0.20	0.24	0.22	0.14	0.19	0.23	0.21	0.23	0.22	0.23	0.22	0.24	0.28	0.30	0.20	0.14

Table 38: Speke Hall Pearson Product Moment Correlations – PAHs versus Magnetics

		Ace	Flu	Phe	Anth	Fluanth	Pyrene	Chrysene	Benzoanth	Benzbfluranth	Benzkfluranth	Benzapyre	Indeno123cdpyr	benzghipery	dibenzahanthr	totalpah	TOC
PC	Mean	0.00	0.20	0.12	-0.13	0.16	0.13	0.14	0.09	0.22	0.25	0.25	0.30	0.22	0.359*	0.23	0.408*
S		0.98	0.25	0.51	0.45	0.37	0.47	0.43	0.59	0.20	0.15	0.15	0.08	0.19	0.03	0.18	0.01
PC	Sorting	-0.07	-0.32	-0.32	-0.10	-0.16	-0.14	-0.15	-0.09	-0.05	-0.04	-0.03	0.00	0.00	-0.18	-0.07	-0.06
S		0.69	0.06	0.06	0.57	0.34	0.41	0.39	0.60	0.77	0.81	0.86	0.98	0.99	0.30	0.71	0.72
PC	Skewness	0.08	0.01	0.31	0.30	0.447**	0.420*	0.444**	0.451**	0.428*	0.455**	0.466**	0.504**	0.401*	0.24	0.468**	0.05
S		0.65	0.96	0.07	0.08	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.02	0.17	0.00	0.76
PC	Kurtosis	0.02	0.19	0.340*	0.03	0.401*	0.385*	0.339*	0.361*	0.344*	0.388*	0.405*	0.473**	0.334*	0.31	0.398*	0.20
S		0.91	0.27	0.05	0.88	0.02	0.02	0.05	0.03	0.04	0.02	0.02	0.00	0.05	0.07	0.02	0.26
PC	%Sand	0.06	0.27	0.24	-0.02	0.25	0.22	0.21	0.17	0.26	0.28	0.28	0.31	0.25	0.381*	0.28	0.408*
S		0.72	0.12	0.16	0.93	0.15	0.21	0.22	0.34	0.13	0.10	0.10	0.07	0.15	0.02	0.11	0.02
PC	%Mud	-0.06	-0.27	-0.24	0.02	-0.25	-0.22	-0.21	-0.17	-0.26	-0.28	-0.28	-0.31	-0.25	-0.381*	-0.28	-0.408*
S		0.72	0.12	0.16	0.93	0.15	0.21	0.22	0.34	0.13	0.10	0.10	0.07	0.15	0.02	0.11	0.02
PC	%vcoarse sand	0.23	0.20	0.391*	0.25	0.542**	0.485**	0.517**	0.556**	0.585**	0.620**	0.607**	0.637**	0.549**	0.479**	0.614**	0.17
S		0.19	0.25	0.02	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.34
PC	%coarse sand	-0.04	0.02	0.06	-0.08	0.21	0.19	0.19	0.16	0.30	0.33	0.368*	0.452**	0.31	0.28	0.32	0.465**
S		0.82	0.93	0.71	0.64	0.22	0.28	0.27	0.36	0.08	0.06	0.03	0.01	0.07	0.10	0.06	0.00
PC	%medium sand	-0.08	0.12	-0.08	-0.28	-0.04	-0.06	-0.05	-0.10	0.08	0.10	0.10	0.15	0.11	0.27	0.07	0.439**
S		0.63	0.49	0.64	0.10	0.83	0.75	0.78	0.59	0.64	0.55	0.56	0.38	0.53	0.12	0.69	0.01
PC	%fine sand	0.19	0.349*	0.389*	0.14	0.31	0.28	0.27	0.23	0.25	0.25	0.25	0.23	0.20	0.335*	0.27	0.25
S		0.28	0.04	0.02	0.44	0.07	0.10	0.11	0.18	0.15	0.15	0.15	0.18	0.24	0.05	0.12	0.14
PC	%vfine sand	0.01	-0.12	0.02	0.22	-0.05	-0.02	-0.04	-0.01	-0.18	-0.21	-0.21	-0.26	-0.21	-0.32	-0.17	-0.431**
S		0.97	0.48	0.90	0.20	0.78	0.89	0.80	0.95	0.29	0.23	0.22	0.13	0.23	0.06	0.31	0.01
PC	%vcoarse silt	-0.03	-0.24	-0.16	0.10	-0.17	-0.14	-0.13	-0.09	-0.21	-0.24	-0.24	-0.28	-0.21	-0.361*	-0.22	-0.440**
S		0.85	0.17	0.37	0.56	0.32	0.41	0.45	0.63	0.22	0.17	0.17	0.11	0.23	0.03	0.20	0.01
PC	%coarse silt	-0.03	-0.29	-0.29	-0.01	-0.28	-0.25	-0.24	-0.20	-0.26	-0.28	-0.28	-0.31	-0.23	-0.358*	-0.28	-0.371*
S		0.85	0.09	0.09	0.96	0.10	0.14	0.16	0.24	0.13	0.11	0.10	0.07	0.18	0.03	0.10	0.03
PC	%medium silt	-0.12	-0.32	-0.347*	-0.12	-0.341*	-0.30	-0.30	-0.25	-0.32	-0.336*	-0.341*	-0.360*	-0.29	-0.403*	-0.342*	-0.400*
S		0.49	0.06	0.04	0.51	0.04	0.08	0.08	0.15	0.06	0.05	0.05	0.03	0.10	0.02	0.04	0.02
PC	%fine silt	-0.17	-0.27	-0.338*	-0.13	-0.363*	-0.32	-0.346*	-0.29	-0.375*	-0.390*	-0.387*	-0.384*	-0.345*	-0.423*	-0.389*	-0.359*
S		0.33	0.12	0.05	0.44	0.03	0.06	0.04	0.09	0.03	0.02	0.02	0.02	0.04	0.01	0.02	0.03
PC	%vfine silt	-0.11	-0.27	-0.352*	-0.12	-0.335*	-0.29	-0.32	-0.27	-0.30	-0.32	-0.32	-0.33	-0.26	-0.360*	-0.33	-0.26
S		0.52	0.12	0.04	0.50	0.05	0.09	0.06	0.12	0.08	0.06	0.06	0.06	0.14	0.03	0.06	0.14
PC	%clay	-0.15	-0.32	-0.347*	-0.10	-0.343*	-0.30	-0.29	-0.25	-0.32	-0.340*	-0.344*	-0.367*	-0.28	-0.383*	-0.341*	-0.399*
		0.38	0.06	0.04	0.56	0.04	0.08	0.09	0.14	0.06	0.05	0.04	0.03	0.10	0.02	0.05	0.02

Table 39: Speke Hall Pearson Product Moment Correlations – PAHs versus Grain Size

		Kappa	χ lf	FD%	SIRM	χARM	χARM/SIRM	SIRM/χLF	χARM/χLF	HIRM	HARD%	ARM	SIRM/ARM	Soft	-20mT	-300mT	Soft/χARM
PC	KAPPA	1.00	**0.998****	-0.01	**0.937****	0.550**	-0.17	0.11	-0.07	**0.938****	-0.508**	0.550**	0.13	**0.973****	-0.22	0.508**	0.04
S			**0.00**	0.96	**0.00**	0.00	0.33	0.51	0.68	**0.00**	0.00	0.00	0.45	**0.00**	0.19	0.00	0.82
PC	χLF	**0.998****	1.00	0.04	**0.937****	0.538**	-0.19	0.11	-0.09	**0.938****	-0.514**	0.538**	0.15	**0.972****	-0.23	0.514**	0.06
S		**0.00**		0.81	**0.00**	0.00	0.27	0.52	0.60	**0.00**	0.00	0.00	0.38	**0.00**	0.18	0.00	0.75
PC	FD%	-0.01	0.04	1.00	0.06	-0.07	-0.23	0.05	-0.17	0.06	-0.22	-0.07	0.25	-0.02	-0.23	0.22	0.14
S		0.96	0.81		0.73	0.67	0.18	0.79	0.32	0.72	0.21	0.67	0.13	0.89	0.18	0.21	0.42
PC	SIRM	**0.937****	**0.937****	0.06	1.00	**0.747****	0.04	0.446**	0.18	**1.000****	-0.473**	**0.747****	-0.06	**0.930****	-0.478**	0.473**	-0.18
S		**0.00**	**0.00**	0.73		**0.00**	0.84	0.01	0.28	**0.00**	0.00	**0.00**	0.74	**0.00**	0.00	0.00	0.30
PC	χARM	0.550**	0.538**	-0.07	**0.747****	1.00	0.675**	**0.745****	**0.782****	**0.744****	-0.20	**1.000****	-0.653**	0.528**	**-0.768****	0.20	**-0.732****
S		0.00	0.00	0.67	**0.00**		0.00	**0.00**	**0.00**	**0.00**	0.25	**0.00**	0.00	0.00	**0.00**	0.25	**0.00**
PC	χARM/SIRM	-0.17	-0.19	-0.23	0.04	0.675**	1.00	0.572**	**0.967****	0.03	0.32	0.675**	**-0.975****	-0.20	-0.606**	-0.32	**-0.954****
S		0.33	0.27	0.18	0.84	0.00		0.00	**0.00**	0.86	0.06	0.00	**0.00**	0.24	0.00	0.06	**0.00**
PC	SIRM/χLF	0.11	0.11	0.05	0.446**	**0.745****	0.572**	1.00	**0.751****	0.443**	-0.04	**0.745****	-0.527**	0.17	**-0.760****	0.04	-0.621**
S		0.51	0.52	0.79	0.01	**0.00**	0.00		**0.00**	0.01	0.82	**0.00**	0.00	0.33	**0.00**	0.82	0.00
PC	χARM/χLF	-0.07	-0.09	-0.17	0.18	**0.782****	**0.967****	**0.751****	1.00	0.18	0.21	**0.782****	**-0.924****	-0.09	**-0.719****	-0.21	**-0.937****
S		0.68	0.60	0.32	0.28	**0.00**	**0.00**	**0.00**		0.30	0.22	**0.00**	**0.00**	0.61	**0.00**	0.22	**0.00**
PC	HIRM	**0.938****	**0.938****	0.06	**1.000****	**0.744****	0.03	0.443**	0.18	1.00	-0.492**	**0.744****	-0.05	**0.930****	-0.476**	0.492**	-0.17
S		**0.00**	**0.00**	0.72	**0.00**	**0.00**	0.86	0.01	0.30		0.00	**0.00**	0.77	**0.00**	0.00	0.00	0.32
PC	HARD %	-0.508**	-0.514**	-0.22	-0.473**	-0.20	0.32	-0.04	0.21	-0.492**	1.00	-0.20	-0.340*	-0.476**	0.12	**-1.000****	-0.26
S		0.00	0.00	0.21	0.00	0.25	0.06	0.82	0.22	0.00		0.25	0.04	0.00	0.49	**0.00**	0.13
PC	ARM	0.550**	0.538**	-0.07	**0.747****	**1.000****	0.675**	**0.745****	**0.782****	**0.744****	-0.20	1.00	-0.653**	0.528**	**-0.768****	0.20	**-0.733****
S		0.00	0.00	0.67	**0.00**	**0.00**	0.00	**0.00**	**0.00**	**0.00**	0.25		0.00	0.00	**0.00**	0.25	**0.00**
PC	SIRM/ARM	0.13	0.15	0.25	-0.06	-0.653**	**-0.975****	-0.527**	**-0.924****	-0.05	-0.340*	-0.653**	1.00	0.16	0.568**	0.340*	**0.973****
S		0.45	0.38	0.13	0.74	0.00	**0.00**	0.00	**0.00**	0.77	0.04	0.00		0.36	0.00	0.04	**0.00**
PC	Soft	**0.973****	**0.972****	-0.02	**0.930****	0.528**	-0.20	0.17	-0.09	**0.930****	-0.476**	0.528**	0.16	1.00	-0.13	0.476**	0.09
S		**0.00**	**0.00**	0.89	**0.00**	0.00	0.24	0.33	0.61	**0.00**	0.00	0.00	0.36		0.46	0.00	0.59
PC	-20mT	-0.22	-0.23	-0.23	-0.478**	**-0.768****	-0.606**	**-0.760****	**-0.719****	-0.476**	0.12	**-0.768****	0.568**	-0.13	1.00	-0.12	**0.736****
S		0.19	0.18	0.18	0.00	**0.00**	0.00	**0.00**	**0.00**	0.00	0.49	**0.00**	0.00	0.46		0.49	**0.00**
PC	-300mT	0.508**	0.514**	0.22	0.473**	0.20	-0.32	0.04	-0.21	0.492**	**-1.000****	0.20	0.340*	0.476**	-0.12	1.00	0.26
S		0.00	0.00	0.21	0.00	0.25	0.06	0.82	0.22	0.00	**0.00**	0.25	0.04	0.00	0.49		0.13
PC	Soft/ARM	0.04	0.06	0.14	-0.18	**-0.732****	**-0.954****	-0.621**	**-0.937****	-0.17	-0.26	**-0.733****	**0.973****	0.09	**0.736****	0.26	1.00
S		0.82	0.75	0.42	0.30	**0.00**	**0.00**	0.00	**0.00**	0.32	0.13	**0.00**	**0.00**	0.59	**0.00**	0.13	
PC	Soft/FD%	0.19	0.20	0.25	0.18	0.09	-0.11	-0.02	-0.08	0.18	-0.20	0.09	0.12	0.19	-0.01	0.20	0.11
S		0.28	0.25	0.16	0.30	0.61	0.52	0.90	0.64	0.30	0.26	0.61	0.49	0.28	0.96	0.26	0.55
PC	χARM/FD%	0.19	0.20	0.25	0.18	0.09	-0.11	-0.02	-0.08	0.18	-0.20	0.09	0.12	0.19	-0.01	0.20	0.11
S		0.28	0.25	0.16	0.30	0.61	0.52	0.90	0.64	0.30	0.26	0.61	0.49	0.28	0.96	0.26	0.55

Table 40: Speke Hall Pearson Product Moment Correlations – Magnetics versus Magnetics

		Kappa	χ l f	F D %	S I R M	χARM	χARM/SIRM	SIRM/χLF	χARM/χLF	HIRM	HARD%	A R M	SIRM/ARM	S o f t	-20mT	-300mT	Soft/χARM
P C	M e a n	-0.14	-0.15	-0.27	-0.10	0.19	0.495**	0.10	0.414*	-0.11	0.421*	0.19	-0.541**	-0.16	-0.15	-0.421*	-0.495**
S		0.43	0.37	0.11	0.57	0.29	0.00	0.58	0.01	0.54	0.01	0.29	0.00	0.36	0.39	0.01	0.00
P C	S o r t i n g	-0.24	-0.24	0.00	-0.13	0.06	0.12	0.27	0.19	-0.13	0.08	0.06	-0.01	-0.23	-0.19	-0.08	-0.05
S		0.17	0.17	0.98	0.47	0.75	0.48	0.12	0.28	0.46	0.64	0.75	0.95	0.19	0.27	0.64	0.79
P C	S k e w n e s s	0.414*	0.399*	-0.23	0.420*	0.428*	0.19	0.22	0.24	0.417*	-0.03	0.428*	-0.16	0.403*	-0.19	0.03	-0.18
S		0.01	0.02	0.19	0.01	0.01	0.28	0.19	0.17	0.01	0.85	0.01	0.36	0.02	0.28	0.85	0.31
PC	K u r t o s i s	0.14	0.12	-0.403*	0.10	0.15	0.19	-0.02	0.15	0.10	0.17	0.15	-0.22	0.15	0.08	-0.17	-0.16
S		0.41	0.48	0.02	0.57	0.40	0.27	0.91	0.38	0.59	0.33	0.40	0.20	0.39	0.64	0.33	0.36
PC	% S a n d	0.03	0.02	-0.24	0.04	0.22	0.410*	0.04	0.33	0.03	0.30	0.22	-0.474**	0.00	-0.14	-0.30	-0.438**
S		0.86	0.93	0.17	0.84	0.20	0.01	0.81	0.05	0.87	0.08	0.20	0.00	1.00	0.43	0.08	0.01
PC	% M u d	-0.03	-0.02	0.24	-0.04	-0.22	-0.410*	-0.04	-0.33	-0.03	-0.30	-0.22	0.474**	0.00	0.14	0.30	0.438**
S		0.86	0.93	0.17	0.84	0.20	0.01	0.81	0.05	0.87	0.08	0.20	0.00	1.00	0.43	0.08	0.01
PC	%vcoarse sand	0.24	0.22	-0.28	0.24	0.30	0.23	0.14	0.25	0.23	0.17	0.30	-0.20	0.20	-0.19	-0.17	-0.21
S		0.17	0.20	0.11	0.17	0.08	0.18	0.41	0.15	0.18	0.32	0.08	0.25	0.24	0.27	0.32	0.22
PC	%coarse sand	-0.07	-0.10	-0.435**	0.02	0.405*	0.665**	0.32	0.626**	0.01	0.440**	0.405*	-0.660**	-0.08	-0.28	-0.440**	-0.618**
S		0.69	0.59	0.01	0.91	0.02	0.00	0.06	0.00	0.95	0.01	0.02	0.00	0.64	0.10	0.01	0.00
PC	%medium sand	-0.362*	-0.375*	-0.21	-0.27	0.12	0.573**	0.14	0.483**	-0.28	0.527**	0.12	-0.608**	-0.381*	-0.20	-0.527**	-0.565**
S		0.03	0.03	0.22	0.11	0.50	0.00	0.41	0.00	0.10	0.00	0.50	0.00	0.02	0.25	0.00	0.00
PC	%fine sand	0.26	0.25	-0.12	0.19	0.13	0.10	-0.13	0.04	0.18	0.04	0.13	-0.19	0.23	0.01	-0.04	-0.16
S		0.13	0.15	0.51	0.28	0.45	0.55**	0.45	0.81**	0.29	0.82**	0.45	0.28	0.19	0.97	0.82**	0.35
PC	%vfine sand	0.29	0.31	0.26	0.21	-0.16	-0.571**	-0.16	-0.495**	0.22	-0.516**	-0.16	0.590**	0.32	0.22	0.516**	0.550**
S		0.09	0.07	0.13	0.22	0.35	0.00**	0.35	0.00**	0.20	0.00**	0.35	0.00**	0.06	0.21	0.00**	0.00**
PC	% vcoarse silt	0.10	0.12	0.25	0.07	-0.20	-0.484**	-0.08	-0.402*	0.08	-0.382*	-0.20	0.537**	0.13	0.17	0.382*	0.495**
S		0.55	0.49	0.15	0.69	0.25	0.00	0.63	0.02	0.66	0.02	0.25	0.00	0.44	0.34	0.02	0.00
P C	%coarse silt	-0.08	-0.07	0.23	-0.04	-0.14	-0.29	0.07	-0.20	-0.04	-0.27	-0.14	0.370*	-0.05	0.03	0.27	0.33
S		0.64	0.70	0.18	0.80	0.42	0.09	0.69	0.24	0.83	0.12	0.42	0.03	0.77	0.85	0.12	0.06
PC	%medium silt	-0.22	-0.20	0.22	-0.20	-0.30	-0.353*	-0.05	-0.29	-0.20	-0.20	-0.30	0.426*	-0.18	0.15	0.20	0.403*
S		0.21	0.24	0.20	0.25	0.08	0.04	0.79	0.09	0.26	0.26	0.08	0.01	0.30	0.38	0.26	0.02
P C	%fine silt	-0.29	-0.28	0.20	-0.28	-0.365*	-0.351*	-0.09	-0.31	-0.28	-0.15	-0.365*	0.414*	-0.25	0.21	0.15	0.410*
S		0.09	0.11	0.25	0.10	0.03	0.04	0.59	0.07	0.11	0.40	0.03	0.01	0.15	0.22	0.40	0.01
PC	%vfine silt	-0.27	-0.25	0.24	-0.22	-0.26	-0.26	0.01	-0.20	-0.22	-0.09	-0.26	0.33	-0.23	0.08	0.09	0.30
S		0.12	0.15	0.17	0.20	0.13	0.14	0.96	0.24	0.21	0.61	0.13	0.05	0.18	0.66	0.61	0.08
PC	% c l a y	-0.19	-0.17	0.30	-0.19	-0.31	-0.381*	-0.10	-0.33	-0.18	-0.23	-0.31	0.450**	-0.17	0.15	0.23	0.418*
		0.28	0.33	0.08	0.28	0.07	0.02	0.58	0.05	0.30	0.19	0.07	0.01	0.33	0.40	0.19	0.01

Table 41: Speke Hall Pearson Product Moment Correlations – Magnetics versus Grain Size

APPENDIX 2

DISEASE INCIDENCE ON MERSEYSIDE

Statistical Analysis of the Health Data and Comparison of the Health Data and Sediment Pollution Data

Hot Spot analysis of the renal and heart disease data was conducted using Arcview GIS to investigate whether there was any significant clustering of the reported incidence. The health and pollutant data were compared using Multinomial logistic regressions (see below) but no statistically significant relationships were found between any of the parameters (data not shown).

Hotspot Analysis

Hotspot Analysis was conducted on the renal disease incidence and the heart disease incidence to try to establish if there was any significant clustering of the data. The Hot Spot analysis was carried out using the inbuilt statistical analysis package found in the Arcview GIS software. The Hot Spot Analysis tool calculates the Getis-Ord Gi* statistic for each feature in the dataset. The resultant z-score indicates where features with either high or low values cluster spatially. The tool works by looking at each feature within the context of neighbouring features. A feature with a high value may not be a statistically significant hot spot. For a Hot Spot to be statistically significant, a feature will have a high value and be surrounded by other features with high values as well. The local sum for a feature and its neighbours is compared proportionally to the sum of all features; when the local sum is much different than the expected local sum, and that difference is too large to be the result of random chance, a statistically significant z- score results. The Gi* statistic returned for each feature in the dataset is a z-score. For statistically significant positive z-scores, the larger the z-score is, the more intense the clustering of high values (hot spot). For statistically significant negative z-scores, the smaller the z-score is, the more intense the clustering of low values (cold spot). The data was plotted in relation to the national average, to show areas where disease incidence was above, equal to or below the national average for each disease (heart disease and renal disease). The disease incidence was compared with the location of each case in the Lower Super Output Area in relation to other cases in the area and the surrounding areas.

Multinomial Logistic Regression

Multinomial logistic regression was used in an attempt to determine a relationship between the cancer data and the pollution data. Data was tested in a variety of ways, including 5-year means. The 5-year means were calculated by dividing the pollution data into 5-year subsets, working backwards from the most recent data, and taking the mean of those data. These data were then processed against the cancer data using multinomial logistic regression (calculated in the statistics package SPSS 16). Multinomial logistic regression is applied in medical research as a method for predicting whether a dependent variable (e.g. cancer incidence) can be explained by the actions of two or more independent variables (e.g. historical pollution data). It will also indicate the relative importance of those independent variables in determining the incidence of the dependent variable. The statistical analysis was carried out a number of times (using both the raw pollution data and the 5-year means) comparing different time periods of the pollution data with the cancer data. This was in an attempt to establish whether there was a time-lag between the pollution appearing in the sediment record and cancer incidence in the area.

No statistically significant relationships were found between the health data and the historical pollution data. The potential reasons for this are discussed in Chapter 11 (see 11.3: Pollutant and Disease Interactions).

Heart and Renal Disease Incidence

The data below illustrate the distribution of heart disease incidence and renal disease incidence on Merseyside. It also shows the location of major industries in the area.

The first map (Fig 64) shows the location of areas that have both below (0.0-1.0) and above (1.0+) the national average incidence of renal (SMR) and heart disease (SAR).

The second map (Fig 65) shows the areas with above national average renal and heart disease incidence in more detail to better distinguish the locations that have a much high percentage of disease incidence.

Approximately two thirds of the Liverpool area has higher than the expected average for heart disease incidence. A Hot Spot analysis was run using the Arcview software and the results indicated that there clustering was occurring and less than 1% of that had occurred by

chance. In epidemiology a cluster of cases is defined as "a collection of cases which are unusually close in time or space or both" (Wilkinson, 2006).

Approximately half of the Warrington area has higher than the expected average for renal disease incidence. A Hot Spot analysis was run and the results showed that, although there was some clustering occurring, most of that was by random chance.

The third map (Fig 66) illustrates the location of 'hotspot' clusters calculated by the Arcview software. The 'hotspot' analysis indicates that there is clustering occurring in heart disease incidence in the north of Liverpool and a small amount in the very south. Renal disease hotspots appear to be located in the centre of the Warrington area.

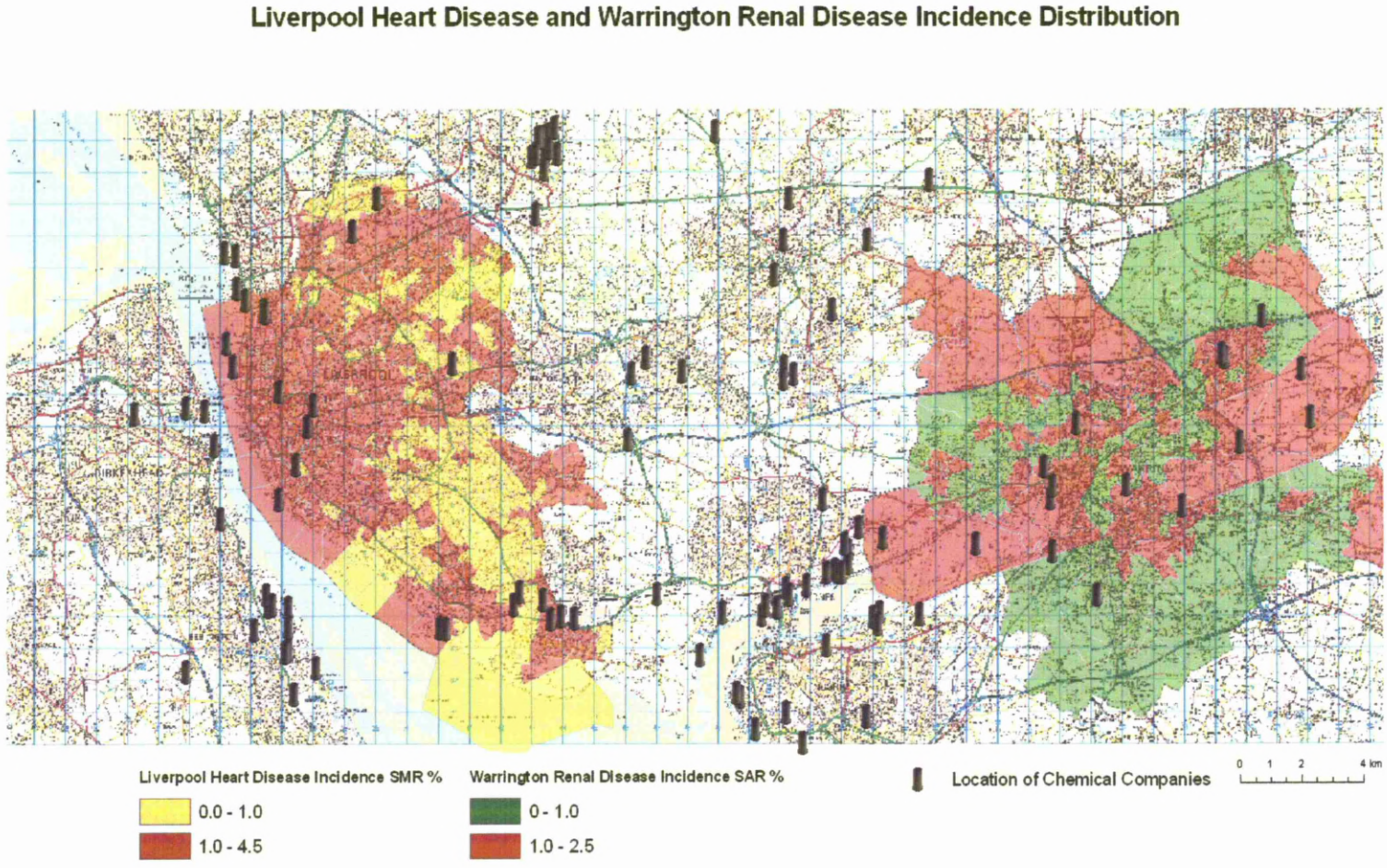


Figure 64: Incidence of Heart Disease and Renal disease below (0.0-1.0) and above (1.0+) the national average. Liverpool Heart Disease Incidence (2003-2005, Under 75 year Olds) and Warrington Renal Disease Incidence (2003-2005. all cases not secondary to other causes)

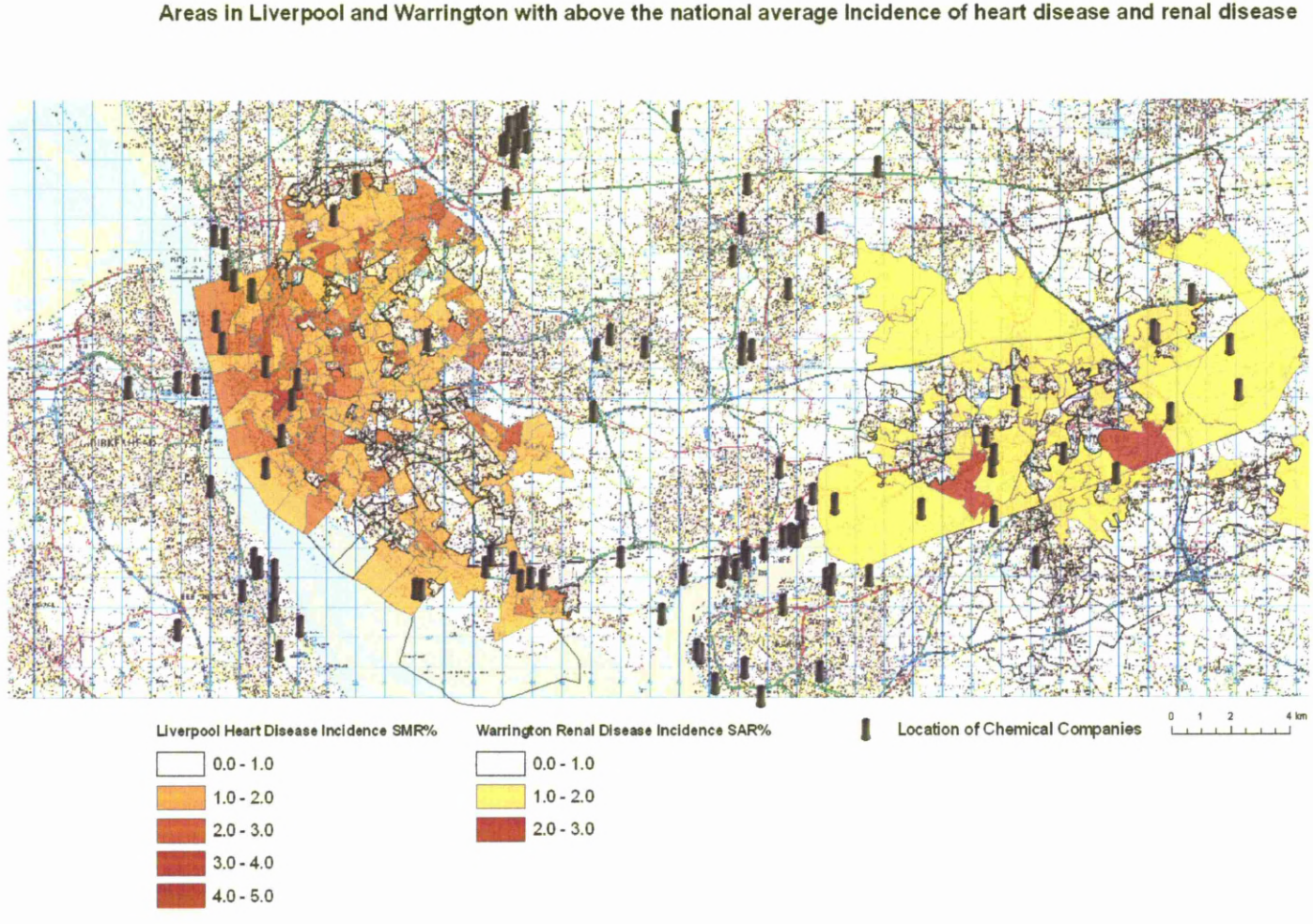


Fig ure 65: Incidence of Heart Disease and Renal disease below (0.0-1.0) and above (1.0+) the national average, comparing areas with highest level in comparison to the average. Liverpool Heart Disease Incidence (2003-2005, Under 75 year Olds) and Warrington Renal Disease Incidence (2003-2005. all cases not secondary to other causes)

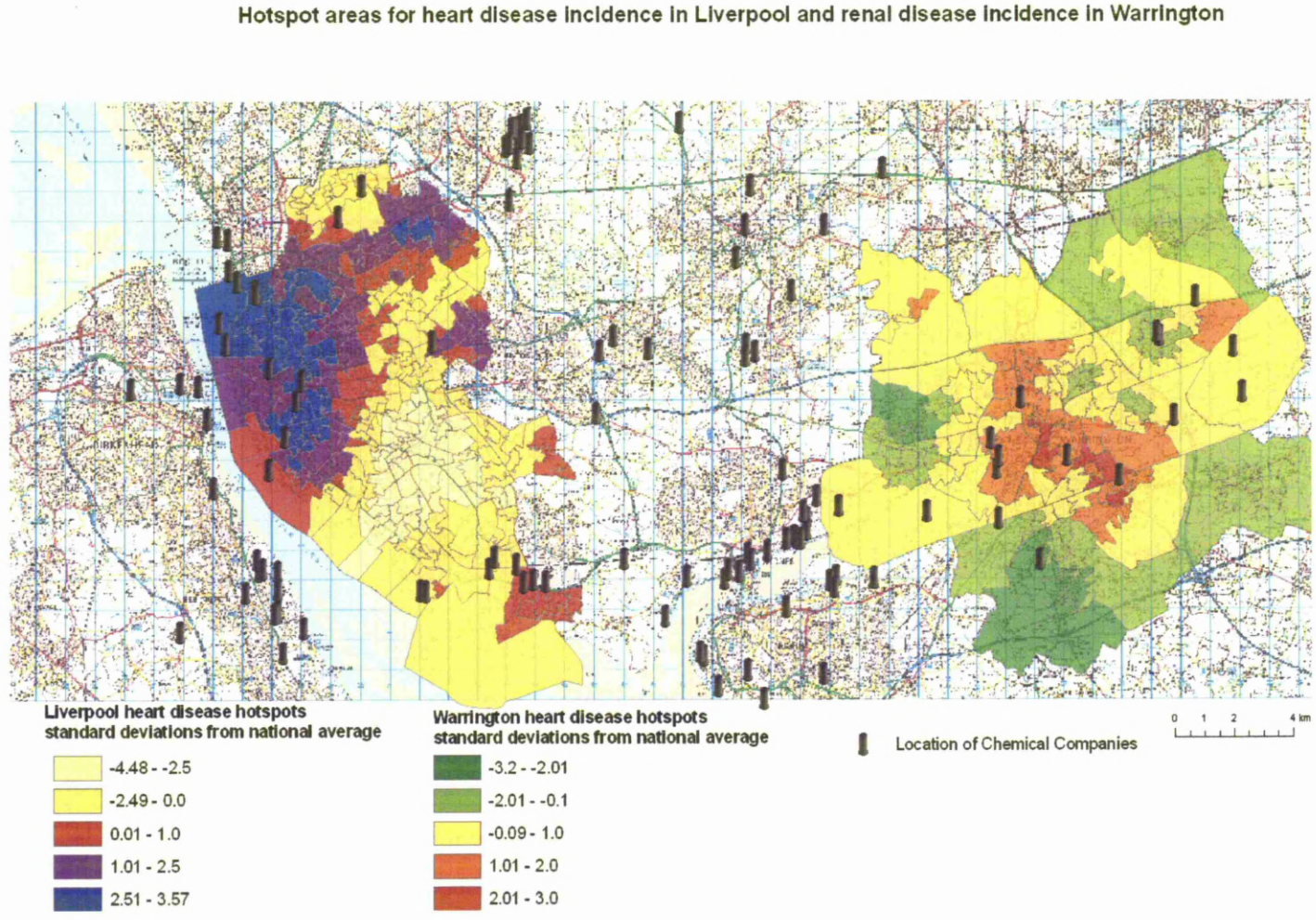


Figure 66: The location of Liverpool heart disease and Warrington renal disease Hot Spots in relation to the National Average. Liverpool Heart Disease Incidence (2003-2005, Under 75 year Olds) and Warrington Renal Disease Incidence (2003-2005. all cases not secondary to other causes)

Areas of Deprivation in Liverpool and Warrington

The maps below indicate the socio-economically most deprived areas of Liverpool and Warrington and these would seem to be approximately the same areas that have high levels of heart and renal disease.

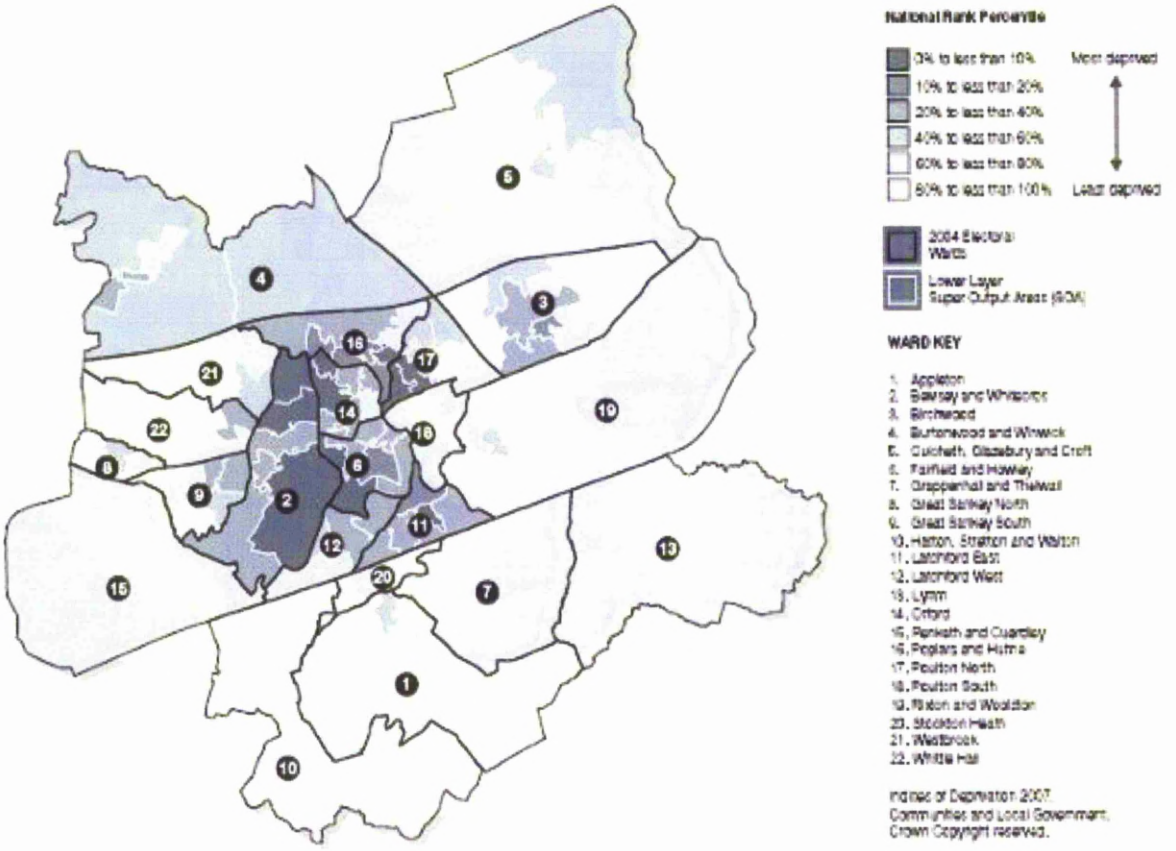


Figure 67: Indices of Deprivation for Warrington 2007. Lower Super Output Areas ranked by national quintile. Taken from The Warrington Partnership website: http://www.warringtonpartnership.org.uk/overview.html

Deprivation is measured by a number of factors including unemployment levels, the percentage of private households not owning a car, the percentage of private households not owner occupied, the percentage of private households with more than one person per room, access to education and disease incidence rates.

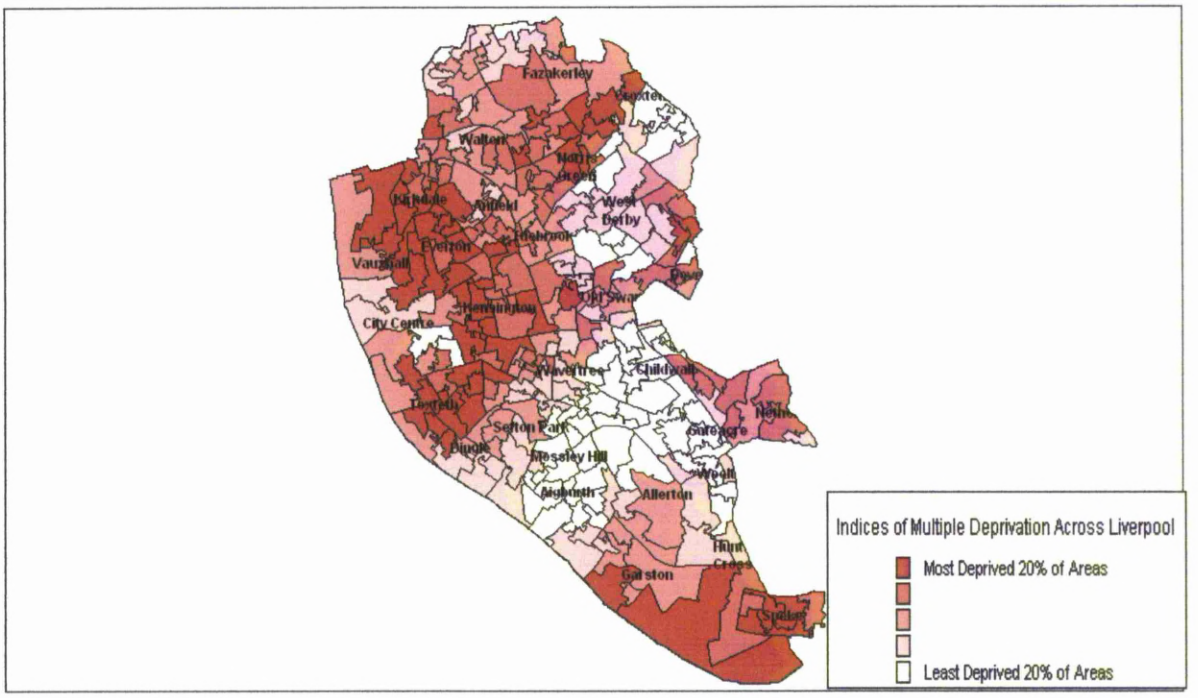


Figure 68: Levels of deprivation in Liverpool (Source: Indices of Deprivation 2004, ODPM, Crown Copyright)

Cancer Incidence in Merseyside and the Surrounding Area

The cancer incidence data for the period from 1993 to 2005 for four combined groups, eleven individual cancers (totals for male and female) and five sex specific cancers for eight areas of Merseyside have been compared with the overall rates of those cancers for Merseyside and Cheshire and England. With the exception of leukemia, kidney cancer, Non Hodgkin Lymphoma, breast cancer, ovarian cancer, uterine cancer and prostate cancer, the combined Merseyside incidence rates are higher (in many cases much higher) than the national average for the same period. In the case of kidney cancer the figures are around the same as those of the national average, whilst for leukaemia and NHL they are lower than the national average

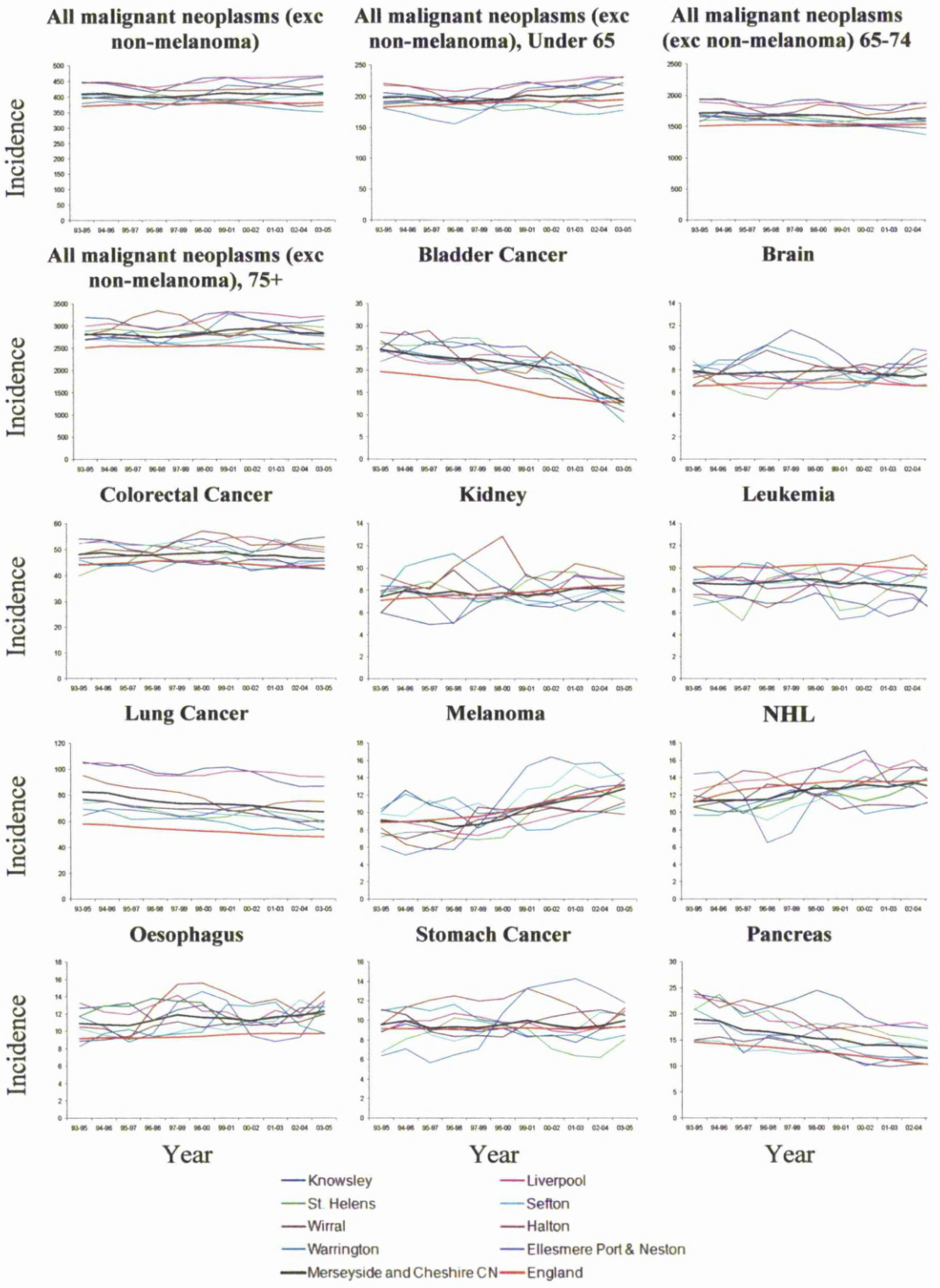


Figure 69: Cancer incidence in the Merseyside area compared with the average for England.

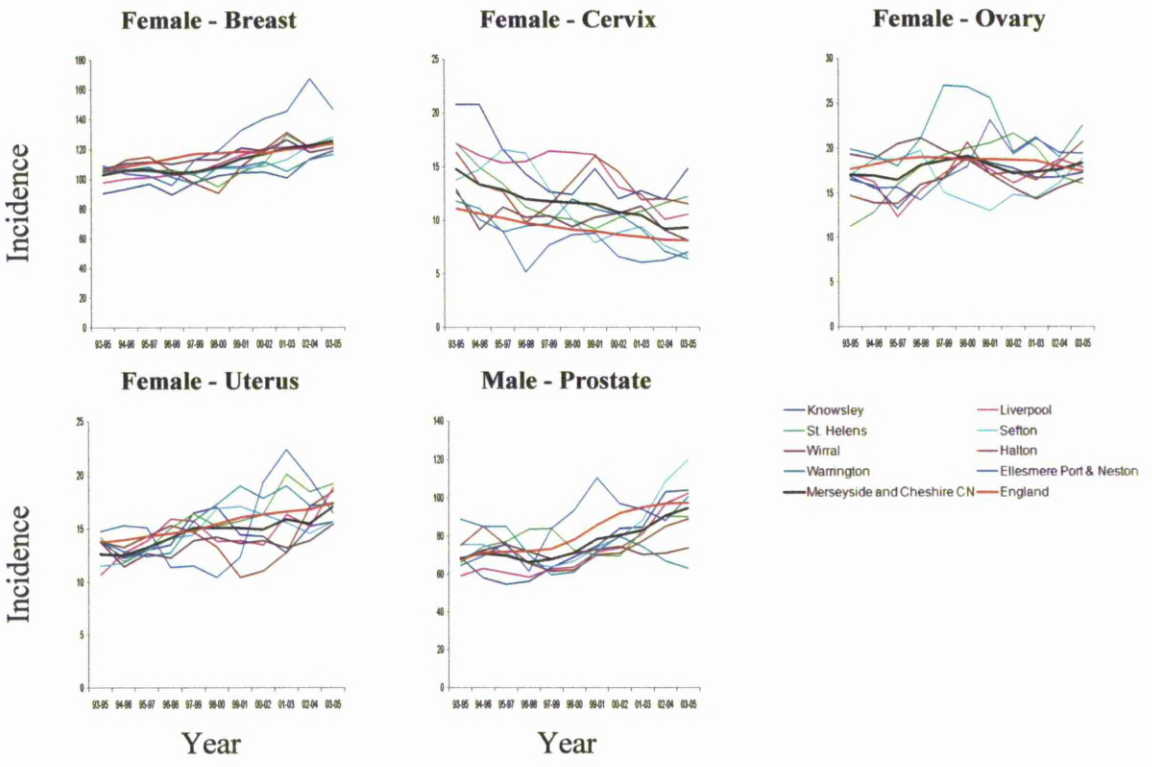


Figure 70: Total sex specific cancer incidence for Merseyside and the surrounding area 1993-2005 compared with the average for England.

DISEASE INCIDENCE ON MERSEYSIDE DISCUSSION POINTS

Heart Disease Incidence and Renal Disease Incidence on Merseyside

Heart disease incidence in Liverpool appears to be located in clusters around the coastal area with relatively high numbers of industrial sites nearby. When considering the prevailing wind conditions, the areas inland from these industries could also be affected by any emissions to the environment. A number of studies have shown links between heart disease and air pollution (Dockery, 1993, Dockery *et al.*, 2001; Roselund *et al.*, 2006). 'Hotspot' analysis does show high levels in areas with clusters of industry. However, these are also the areas of the highest levels of deprivation. Unfortunately, because of the data available for this study, we are unable to identify whether high levels of heart disease in Merseyside are related to pollution or to other factors such as diet, smoking and lifestyle. Atherton (1999) stated that smoking is the single biggest contributor to heart disease on Merseyside.

The areas with the highest incidence of heart disease have been shown, in the past, to have high levels of unemployment (Merseyside Director of Public Health, 1995) and associated

levels of poor health and correspond to the areas with the highest levels of deprivation, leading to the conclusion that socio-economic factors are responsible for much of the heart disease in the Liverpool area. Liverpool Public Health Observatory has shown that levels of heart disease correlate well with indicators of deprivation (LPHO, 1995). Surveys have also shown that the areas in Merseyside with the highest levels of unemployment also tend to have the highest levels of smokers and drinkers and low levels of people who exercise regularly and believe their diet is healthy (LPHO, 1995). A study by Milligan *et al.* (1998) revealed that children living close to the Liverpool docks were twice as likely to suffer from respiratory diseases than children living over 2 km away.

Renal disease in Warrington, although higher than average in several areas, does not appear to show any significant levels of clustering. However, in the 'hotspot' analysis the highest levels are in the centre of the Warrington region in areas of highest deprivation. There are two area of high incidence in the region and both of these have a number of industrial sites surrounding them and, as with heart disease, it is possible that emissions from these industries are being directed at these locations by the prevailing winds (Fig 63).

In both the Liverpool and Warrington areas the higher levels of disease are found in the most socio-economically deprived locations. This means that it is not possible with the level of data available to make a definitive conclusion regarding whether the industry in the location is responsible for the higher levels of disease or whether they are related to the levels of deprivation in these areas. It is likely that there is a combination of the two factors at work, but this cannot be proven in this study. Areas of deprivation often have high levels of disease due to poor diet, high levels of smoking and, in recent years, increasing levels of obesity.

In order to assess the relative contribution of pollution to incidence of heart disease and renal disease we would need more information regarding the subjects of the study. For example, age, sex, socioeconomic status, smoking habits, body mass index, cholesterol, diet, and hypertension. There is also evidence that peri-natal exposure to a variety of pollutants can contribute to disease in adults (Baker, 1995), so information on early childhood and parental data could also be useful indentifying potential causes of disease.

With the renal disease and heart disease data it is not possible to look at long-term disease trends as the data provided was only for 1 year. However, data from annual health reports indicates that Merseyside has considerably higher levels of death from heart disease than the national average (Atherton *et al.*, 1999). Deaths have been decreasing in recent years, but that is probably due to a combination of improved treatment and recent government

campaigns to increase awareness of the causes of heart disease such as obesity, diet and lack of exercise and it is likely that these will have had some influence on the mortality rates.

Cancer Incidence on Merseyside

Cancer is responsible for 1 in 4 deaths in Merseyside (Atherton *et al.*, 1999). In particular, lung cancer rates are much higher than the national average and, whilst there is a drop in the number of men being diagnosed, the rates in woman are not falling and, in certain areas, appear to increasing and some of this is due to larger numbers of girls taking up smoking at an early age (Atherton *et al.*, 1999). Work has shown that the highest levels of smoking on Merseyside correspond to the inner city and urban areas with the highest levels of deprivation (Inequalities in health in the North West, 1998). Breast cancer rates are on the increase nationally and, with the exception of Ellesmere Port, levels in Merseyside are approximately around the national average. This would suggest that there is no regional influence on breast cancer rates.

For the four combined sets of cancer data (All malignant neoplasms, All malignant neoplasms under 65, All malignant neoplasms 65-74 and All malignant neoplasms 75 +) the eight areas in Merseyside have above the national average incidence with the exception of Ellesmere Port (in the early 90s) and Warrington (in recent years) for the under 65 age group. Levels of these cancers have remained relatively stable as have those of colorectal cancer. Bladder cancer, lung cancer and pancreatic cancer incidence appear to be on the decrease, whilst melanoma is increasing and stomach, oesophagus, NHL, leukaemia, kidney and brain cancers do not appear to be exhibiting any obvious trends. Cancers that have above national average incidence for most areas around Merseyside include total cancer incidence, bladder, brain, colorectal, lung, oesophagus and pancreatic cancers. The remaining cancers have levels that fluctuate around the national average. For the sex specific cancers, Merseyside areas seem to be around the national average for all except cervical cancer for which incidence is above national average for most areas.

Colorectal and uterine cancer have been shown to not be affected by levels of deprivation whilst brain, breast, leukaemia, NHL, prostate and testicular cancer rates are higher in less deprived areas. Lung, cervical, oesophagus, bladder, kidney, stomach and pancreatic cancer show positive correlations with deprivation (Quinn *et al.*, 2001).

Of the cancers listed above the following have been shown to have an environmental link (including from occupational/workplace exposure (Bodner *et al.*, 2003)), lung (air pollution)

bladder, brain (including a link with petrochemical exposure) kidney (cadmium and asbestos exposure) NHL and of those bladder, kidney and lung have also been linked with tobacco usages (Schottenfeld, 1996; Quinn *et al.*, 2001).

Other causes of cancer can be tobacco use (Das, 2003), genetics, behavioural e.g. breast, ovarian, and uterine cancer increases have been suggested to be related to a delay in the age of reproduction in the western world (McPherson *et al.*, 1994), dietary (colorectal cancer – Krongborg *et al.*, 1994; Adami and Trichopoulus, 2003), disease (e.g. cervical cancer and the human papillomavirus, Quinn *et al.*, 2001) and even sunbathing and sunburn (including sun bed use) for the increase in melanoma.

One of the main arguments against cancer being an environmental disease is that it is a disease of aging with levels higher in older people (Quinn *et al.*, 2001). However, if levels of some cancers are related to long term chronic exposure (e.g. lung cancer can take 20 years or more to develop in a smoker) then it is to be expected that incidence will be higher amongst the elderly, as they will have been exposed to low levels for a longer period of time.

Socio-economic factors are an important consideration when investigating disease incidence. Socio-economically disadvantaged people tend to live closer to sources of pollution, as these are less desirable areas and, therefore, house prices are usually lower. These groups are, therefore, more likely to be exposed to any potential industrial sources of pollution, which could, at least partially, help to explain the heart disease clustering in the areas of higher deprivation in Liverpool and Warrington. However, these people are also more likely to work in industries where they will be exposed to potential toxic chemicals and poorer people are known to have higher rates of disease, including cancer, due other lifestyle factors such as smoking and poor diet (Wilkinson, 2006).

A report in 1990 on pollution and health in Merseyside showed a direct correlation in overall SMR and the proportion of industrialised land in the area (Hussey *et al.*, 1990). This study controlled for socio-economic factors and still showed higher levels of mortality in industrial areas of Merseyside. The study also raised the issue that as well as known sources of industrial pollution, there are many landfill sites in the region which could be contributing to the pollutant load. This study also found a consistent trend of higher levels of cancer associated with areas containing a high proportion of industrialised land (although this was not statistically significant).

It still remains a fact that the Merseyside area has higher levels of most major cancers than the national average and, in some cases, other similarly industrialised and deprived regions (Fig 71). There are many reasons why this could be the case, including the levels of industry. However, with the data available it is not possible to assign blame purely to the industrial history of the region.

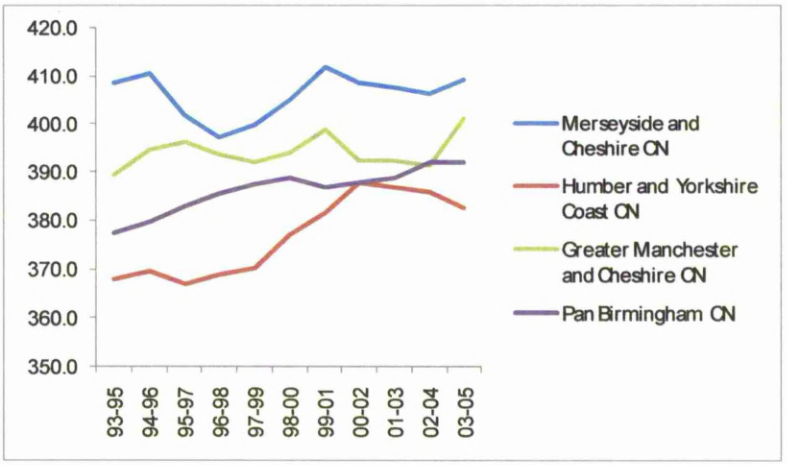


Figure 71: Comparison of cancer incidence (all malignant neoplasms) for selected industrialised areas of the UK.

REFERENCES

Abarnou, A., Avoine, J., Dupont, J.P., Lafite, R. and Simon, S. (1987) Role of suspended sediments on the distribution of PCB in the Seine Estuary (France). *Continental Shelf Research.* 7, 1345-1350

Abramowicz, D.A., Brennan, M.J., Van Dort. H.M. and Gallagher, E.L. (1993) Factors influencing the rate of polychlorinated biphenyl dechlorination in Hudson river sediments. *Environmental Science and Technology* **27**, 1125-1131

Abu-Saba, O. and Al-Madafa, H. (1997) Chromium distribution in waters and sediments of the eastern side of the Qatari Peninsula. *Science of the Total Environment* **196**, 1-11

Achterberg, E.P., Van Den Berg, C.M.G. (1996) Automated monitoring of Ni, Cu and Zn in the Irish Sea. *Marine Pollution Bulletin* **32,** 471-479

Adami, H.O., Trichopoulos, D. (2003) Obesity and mortality from cancer. *New England Journal of Medicine* **348,** 1623-1624

Airey, D., Jones, P.D. (1982) Mercury in the river Mersey, its estuary and tributaries during 1973 and 1974. *Water Research* **16,** 565-577

Alcock, R.E., Johnston, A.E., McGrath, S.P., *et al.* (1993) Long-term changes in the polychlorinated biphenyl content of united-kingdom soils. *Environmental Science & Technology* **27,** 1918-1923

Alcock, R.E., Halsall, C.J., Harris, C.A., Johnston, A.E., Lead, W.A., Sanders, G. and Jones, K.C. (1994) Contamination of environmental samples prepared for PCB analysis. *Environmental Science and Technology* **28**, 1838-1842

Allen, J.R.L. (2000) Morphodynamics of Holocene saltmarshes: a review sketch from the Atlantic and Southern North Sea coasts of Europe. *Quaternary Science Reviews* **19,** 1155

Amin, S., Huie, K., Hecht, S. (1985). Mutagenicity and tumor-initiating activity of methylated benzo(b)fluoranthenes. *Carcinogenesis* **6**: 1023-1025.

Araujo, M.F.D., Bernard, P.C. and Van Greiken, R.E. (1988) Heavy metal contamination in sediments from the Belgian coast and Scheldt estuary. *Marine Pollution Bulletin* **19**, 269-273

Aston, S.R. and Chester, R. (1973) The influence of suspended particles on the precipitation of iron in natural waters. *Estuarine, Coastal and Marine Science* **1**, 225-231

Aston, S., (1983) Natural Water and Atmospheric Chemistry of Silicon. In: S. Aston (Ed.), Silicon Geochemistry and Biogeochemistry. Academic Press, London, 77-100

Atherton, J., Forrest, D., Husseey, R., Reid, J. (1999) Mesrseyside's health 1999. The annual report of the directors of public health on Merseyside

Atkinson, C.A., Jolley, D.F., Simpson, S.L. (2007) Effect of overlying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from metal contaminated marine sediments. *Chemosphere* **69,** 1428-1437

Audry, S., Schafer, J., Blanc, G. and Jouanneau, J. (2004) Fifty year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot river reservoirs (France). *Environmental Pollution* **132,** 413-426

Aydin, M.E., Ozcan, S., Tor, A. (2007) Ultrasonic solvent extraction of persistent organic pollutants from airborne particles. *Clean-Soil Air Water* **35,** 660-668

Azimi, S., Rocher, V., Muller, M. *et al.* (1997) Sources, distribution and variability of hydrocarbons and metals in atmospheric deposition in an urban area (Paris, France). *Science of the Total Environment* **337,** 223-239

Baker, J.E., Capel, P.D. and Eisenreich, S.J. (1986) Influence of colloids in sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. *Environmental Science and Technology.* **20,** 1136-1143

Ball, D.F. (1964) Loss-on-ignition as an estimate of organic matter and organic carnbon in non-calcareous soils. *Journal of Soil Science* **15,** 84-92

Balls, P.W. (1989) The partition of trace metals between dissolved and particulate phases in European coastal waters. A compilation of field data and comparison with laboratory studies. *Netherlands Journal of Sea Research* **23,** 7-14

Banjoo, D.R. and Nelson, P.K. (2005), Comparison of ultrasonic and pressurized liquid extraction for the analysis of polycyclic aromatic compounds in soil samples by gas chromatography coupled to tandem mass spectrometry. *Journal of Chromatography A* **1066**

Banjoo, D.R., Nelson, P.K. (2005): Improved ultrasonic extraction procedure for the determination of polycyclic aromatic hydrocarbons in sediments. *Journal of Chromatography A* **1066** 9-18

Barco-Bonilla, N., Vidal, J. L., Martinez, Garrido Frenich, A, *et al.*(2009) Comparison of ultrasonic and pressurized liquid extraction for the analysis of polycyclic aromatic compounds in soil samples by gas chromatography coupled to tandem mass spectrometry *Talanta* **78,** 156-64

Barker, D. J. P. (1995) Fetal origins of coronary heart disease. *British Medical Journal* **311,** 171-174

Barra, R., Cisternas, M., Suarez, C., Araneda, A., Pinones, O. and Popp, P. (2004) PCBs and HCHs in a salt-marsh sediment record from South-Central Chile: use of tsunami signatures and ^{137}Cs fallout as temporal markers. *Chemosphere* **55,** 965-972

Bartlett, P.D., Craig, P.J. (1981) Total mercury and methyl mercury levels in british estuarine sediments. *Water Research* **15,** 37-47

Bartlett and James, (1980). Studying dried stored soil samples – some pitfalls soil. *Science Society America Journal* **44,** 721

Bates, M.N., Smith, A.H. and Hopenhayn-Rich, C. (1992) Arsenic ingestion and internal cancers: a review. *American Journal of Epidemiology.* **135,** 462-476.

Bazylinski, D.A., Frankel, R.B. and Jannasch, H.W. (1988) Anaerobic magnetite production by a marine magnetotactic bacterium. *Nature* **334,** 518-519

Beckwith, P.R., Ellis, J.B., Revitt, D.M. and Oldfiled, F. (1986) Heavy metal and magnetic relationships for urban source sediments. *Physics of the Earth and Planetary Interiors* **42**, 67-75

Beeftink, W.G., Nieuwenhuize, J., Stoeppler, M and Mohl, C. (1982) Heavy metal accumulation in saltmarshes from the western and eastern Scheldt. *Science of the Total Environment* **25**, 199-223

Belzile,N., Chen,Y.W,, Gunn,J.M. *et al.*(2004) Sediment trace metal profiles in lakes of Killarney Park, Canada: from regional to continental influence. *Environmental Pollution* **130,** 239-248

Belzile, N., Lebel, J. (1986) Capture of arsenic by pyrite in near-shore sediments. *Chemical Geology* **54**, 279-281

Belzile, N., Tessier, A. (1990) Interactions between arsenic and iron oxyhydroxides in natural sediments. *Geochimica et Cosmochimica Acta* **54**, 103-109.

Bendell-Young, L. I., Harvey, H. H., Dillon P J. and Smith P. J. (1989) Contrasting behaviour of Mn in the surficial sediments of 13 south-central Ontario lakes. *Science of the Total Environment.* **87/88**, 129-139.

Benlahcen, K.T., Chaoui, A., Budzinski, H. *et al.* (1997) Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. *Marine Pollution Bulletin* **34,** 298-305

Bernes Claes (1998) English Translation by Martin Naylor. Persistent Organic Pollutants: A Swedish View of an International Problem. Swedish Environmental Protection Agency

Berry, A. and Plater, A.J. (1998) Rates of tidal sedimentation from records of industrial pollution and environmental magnetism: the Tees estuary, north-east England. *Water Air and Soil Pollution* **106,** 463-479

Beuskens, J.E.M., Mol, G.A.J., Barreveld, H.L., Vanmuster, B. and Winkels, H.J. (1991) Geochronology of priority pollutants in a sedimentation area of the Rhine river. *Environmental Contamination and Toxicology* **12**, 1549-1566

Blais, J.M., Kalff, J. (1993) Atmospheric loading of Zn, Cu, Ni, Cr, and Pb to lake-sediments - the role of catchment, lake morphometry, and physicochemical properties of the elements. *Biogeochemistry* **23**, 1-22

Blais, J.M., Kalff, J. (1995) The influence of lake morphometry on sediment focusing. *Limnology and Oceanography* **40,** 582-588

Blott, S.J., Pye, K. (2001) gradistat: a grain size distribution and statistics package for the analysis of unconsolidated sediments. *Earth Surface Processes and Landforms* **26**: 1237-1248

Blott, S.J., Pye, K., Van der Wal, D. *et al.* (2006) Long-term morphological change and its causes in the Mersey Estuary, NW England. *Geomorphology* **81** 185-206

Bluhm, R.E., Breyer, J.A., Bobbitt, R.G. *et al.* (1992) Elemental mercury-vapor toxicity, treatment, and prognosis after acute, intensive exposure in chloralkali plant workers .2. hyperchloremia and genitourinary symptoms. *Human & Experimental Toxicology* **11.** 211-215

Blumer, M. (1957) Removal of Elemental Sulfer from hydrocarbon fractions. *Analytical Chemistry* **29**, 1039

Bodner, K.M., Collins, J.J., Bloemen, L.J. *et al.* (2003) Cancer risk for chemical workers exposed to 2,3,7,8-tetrachlorodibenzo-p-dioxin. *Occupational and Environmental Medicine* **60,** 672-675

Boogaard, P.J., Houtsma, A.T.A.J., Journee, H.L. *et al.* (1996) Effects of exposure to elemental mercury on the nervous system and the kidneys of workers producing natural gas. *Archives of Environmental Health* **51,** 108

Borja, J., Taleon, D.M., Auresenia, J. *et al.* (2005). Polychlorinated biphenyls and their biodegradation. *Process Biochemistry* **40,** 1999-2013

Borgert, C.J. (2004) Chemical mixtures: An unsolvable riddle? *Human and Ecological Risk Assessment* **10,** 619-629

Borgert, C.J., Quill, T.F., McCarty, L.S, *et al.* (2004) Can mode of action predict mixture toxicity for risk assessment? *Toxicology and Applied Pharmacology* **201,** 85-96

Boudreau, B.P. (1999) Metals and models: diagenetic modelling in freshwater lacustrine sediments. *Journal of Paleolimnology* **22,** 227-251

Boughriest, A., Oudane, B., Fischer, J.C., Wartel, M. and Leman, G. (1992) Variability of dissolved Mn and Zn in the Seine estuary and chemical speciation of these metals in suspended matter. *Water Research* **26**, 1359-1378

Bouloubassi, I., Saliot, A. (1993) dissolved, particulate and sedimentary naturally derived polycyclic aromatic-hydrocarbons in a coastal environment - geochemical significance. *Marine Chemistry* **42**, 127-143

Boyle, E.A., Edmond, J.M. and Sholkovitz, E.R. (1977) The mechanism of iron removal in estuaries. *Geochimica et Cosmochimica Acta* **41**, 1313-1324

Boyle, J. (1995) A simple closure mechanism for a compact, large-diameter, gravity corer. *Journal of Paleolimnology* **13**, 85-87

Boyle J.F. (2000) Rapid elemental analysis of sediment samples by isotope source XRF. *Journal of Paleolimnology* **23**, 213–221

Boyle. J.F. (2001) Redox remobilization and the heavy metal record in lake sediments: a modelling approach. *Journal of Paleolimnology* **26,** 423-431

Boyle. J.F. (2001) Inorganic geochemical methods in palaeolimnology. In: W.M. Last and J.P. Smol ed(s). Tracking environmental change using lake sediments: physical and chemical techniques. Dordrecht, Kluwer Academic

Breivik, K., Sweetman, A., Pacyna, J.M. *et al.* (2002) Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 1. Global production and consumption. *Science of the Total Environment* **290,** 181-198

British Geological Survey (1997) Regional geochemistry of parts of north west England and North Wales. BGS Nottingham

Brody, J.G., Rudel, R.A., Michels, K.B. *et al.* (2007) Environmental pollutants, diet, physical activity, body size, and breast cancer - Where do we stand in research to identify opportunities for prevention? *Cancer* **109,** 2627-2634

Brownawell, B. and Farrington, J. (1986) Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment. *Geochimica et Cosmochimica Acta.* **50**, 157-169

Bryan, G.W., Langston, W.J. (1992) Bioavailability, accumulation and effects of heavy metals in sediments, with special reference to United Kingdom estuaries – a review. *Environmental Pollution* **76**, 89-131

Budzinski, H., Jones, I., Bellocq, J. *et al.* (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry* **58,** 85-97

Buckley, D.E., Smith, J.N. and Winters, G.V. (1995) Accumulation of contaminant metals in marine sediments of Halifax Harbour, Nova Scotia: environmental factors and historical trends. *Applied Geochemistry* **10**, 175-195

Buonanno, G., Ficco, G., Stabile, L. (2009) Size distribution and number concentration of particles at the stack of a municipal waste incinerator. *Waste Management* **29,** 749-755

Burton, L.R. (2003) The Mersey Basin: an historical assessment of water quality from an anecdotal perspective. *The Science of the Total Environment* **314-316**, 53-66

Cacador, I., Vale, C. and Catarino, F. (1996) Accumulation of Zn, Pb, Cu, Cr, and Ni in sediments between roots of the Tagus Estuary saltmarshes, Portugal. *Estuarine, Coastal and Shelf Science* **42**, 393-403

Cailleaud, K., Forget-Leray, J., Souissi, S. *et al.* (2007) Seasonal variations of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species Eurytemora affinis (Calanoida, copepoda). Part 1: PCBs and PAHs. *Chemosphere* **70**. 270-280

Callender, E. (2000) Geochemical effects of rapid sedimentation in aquatic systems: minimal diagenesis and the preservation of historical metal signatures. *Journal of Paleolimnology* **23,** 243-260

Calmano, W. and Forstner, U. (1983) Chemical extraction of heavy metals in polluted river sediments in central Europe. *The Science of the Total Environment* **28**, 77-90.

Camacho-Ibar, V.F., Wrench, J.J., Head, P.C. (1992) Contrasting Behavior of Arsenic and Mercury in Liverpool Bay Sediments. *Estuarine Coastal and Shelf Science* **34,** 23-36

Camacho-Ibar, V.F. and McEvoy, J. (1996) Total PCBs in Liverpool Bay sediments. *Marine Environmental Research* **41**, 241-263

Campbell, J.A., Chan, E.Y.L., Riley, J.P. *et al.* (1986) The distribution of mercury in the Mersey estuary. *Marine Pollution Bulletin* **17,** 36-40

Campbell, J.A., Whitelaw, K., Riley, J.P., Head, P.C. and Jones, P.D. (1988) Contrasting behaviour of dissolved and particulate nickel and zinc in a polluted estuary. *The Science of the Total Environment* **71**, 145-155

Canfield, R.L., Henderson, C.R., Deborah, M.A., Cory-Slechta, A., Cox, C., Jusko, T.A., and Lanphear, B., M.P.H. (2003) Intellectual Impairment in Children with Blood Lead Concentrations below 10 μg per Deciliter. *New England Journal of Medicine* **348**, 16

Caricchia, A.M., Chiavarini, S. Pezza, M. (1999) Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmospheric Environment* **33,** 3731-3738

Carignan, R., Tessier, A. (1985) Zinc deposition in acid lakes - the role of diffusion. *Science* **228**, 1524-1526

Cauwet, G. (1987) Influence of sedimentological features on the distribution of trace metals in marine sediments. *Marine Chemistry* **22**, 221-234

Cavalieri, E.l., Rogan, E., Cremonesi, P. *et al.* (1988) Tumorigenicity of 6-halogenated derivatives of benzo[a]pyrene in mouse skin and rat mammary gland. *Journal of Cancer Research and Clinical Oncology* **114**, 10-15

CCME (Canadian Council of Ministers of the Environment) (1995) Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life. CCME EPC-98E. Prepared by Environment Canada, Guidelines Division, Technical Secretariat of the CCME Task Group on Water Quality Guidelines, Ottawa.[Reprinted in Canadian environmental quality guidelines, Chapter 6,Canadian Council of Ministers of the Environment, 1999, Winnipeg.

Chan, L.S., Ng, S.L., Davies, A.M., Yim, W.W.S. and Yeung, C.H. (2001) Magnetic properties and heavy metal contents of contaminated seabed sediments of Penny's Bay, Hong Kong. *Marine Pollution Bulletin* **42**, 569-583

Chan, L.S., Yeung, C.H., Yim, W.W.S. and Or, O.L. (1998) Correlation between magnetic susceptibility and distribution of heavy metals in contaminated sea-floor sediments of Hong Kong harbour. *Environmental Geology* **36**, 77-86

Chang, B.V., Liu, W.G., Yuan, S.Y. (2001) Microbial dechlorination of three PCB congeners in river sediment. *Chemosphere* **45**, 849-856.

Charlesworth, S.M., Foster, I.D.L. (1999) Sediment budgets and metal fluxes in two contrasting urban lake catchments in Coventry, UK. *Applied Geography* **19,** 199-210

Charlesworth, S.M., Lees, J.A. (2001) The application of some mineral magnetic measurements and heavy metal analysis for characterising fine sediments in an urban catchment, Coventry, UK. *Journal of Applied Geophysics* **48,** 113-125

Charlesworth, M.E., Chenery, S., Mellor, A. *et al.* (2006) Isotopic composition and concentration of Pb in suspended particulate matter of the Irish Sea reveals distribution and sources. *Marine Pollution Bulletin* **52,** 81-88

Chen, C.J., Chen, C.W., Wu, M.M.and Kuo, T.L. (1992) Cancer potential in liver lung, bladder and kidney due to ingested inorganic arsenic in drinking water. *British Journal of Cancer* **66**, 888-892

Chiou, H.Y., Hsueh, Y.M., Liaw, K.F., Horng, S.F., Chiang, M.H., Pu, Y.S., Lin, J.S. Huang, C.H., and Chen, C.J. (1995) Incidence of internal cancers and ingested inorganic arsenic: a seven-year follow-up study in Taiwan. *Cancer Research.* **55**, 1296-1300

Collings, S.E., Johnson, M.S., Leah, R.T. (1996) Metal contamination of angler-caught fish from the Mersey Estuary. *Marine Environmental Research* **41,** 281-297

Colman, S.M. and Bratton, J.F (2003) Anthropogenically induced changes in sediment and biogenic silica fluxes in Chesapeake Bay. *Geology*, **31**, 71-74

Columbo, M.J., Khalil, M.F., Arncac, M., Horth, A. and Cattoggio, J.A. (1990) Distribution of chlorinated pesticides and individual polychlorinated biphenyls in biotic and abiotic compartments of the Rio de la Plata. *Environmental Science and Technology* **24**, 498-505

Comber, D.P.M., Hansom, J.D., Fahy, F.M. (1993). Estuaries Management Plans: Coastal Processes and Conservation—Mersey Estuary. University of Glasgow, Glasgow.

Coomber, S.D.W., Gunn, A.M. and Whalley, C. (1995) Comparison of the partitioning of trace metals in the Humber and Mersey estuaries. *Marine Pollution Bulletin* **30**, 851-860

Craig, P.J., Morton, S.F. (1976) Mercury in Mersey estuary sediments, and analytical procedure for total mercury. *Nature* **261,** 125-126

Cundy, A.B. and Croudace, I.W. (1995) Sedimentary and geochemical variations in a saltmarsh / mud flat environment from the mesotidal Hamble estuary, southern England. *Marine Chemistry* **51**, 115-132

Cundy, A.B., Croudace, I.W., Thomson, J. *et al.* (1997) Reliability of saltmarshes as "geochemical recorders" of pollution input: A case study from contrasting estuaries in southern England. *Environmental Science and Technology* **31,** 1093-1101

Cundy, A.B., Croudace, I.W., Cearreta, A. *et al.* (2003) Reconstructing historical trends in metal input in heavily-disturbed, contaminated estuaries: studies from Bilbao, Southampton Water and Sicily. *Applied Geochemistry* **18** 311-325

Damstra, T. (2002) Potential effects of certain persistent organic pollutants and endocrine disrupting chemicals on the health of children. *Journal Of Toxicology-Clinical Toxicology* **40**, 457-465

Darvill, T., Lonky, E., Reihman, J., Stewart, P., Pagano, J. (2000) Prenatal exposure to PCBs and infant performance on the Fagan Test of Infant Intelligence. *Neurotoxicology* **21**, 1029-1038

Das, S.K. (2003) Harmful health effects of cigarette smoking. *Molecular and Cellular Biochemistry* **253,** 159-165

Davidson, C.M., Gibson, M.D., Hamilton, E. *et al.* (2005) The long-term environmental behaviour of strontium and barium released from former mine workings in the granites of the Sunart region of Scotland, UK. *Chemosphere* **58,** 793-798

Davies, N.J. and Wolff, G.A. (1990) The Mersey oil spill, August 1989. A case of sediments contaminating the oil? *Marine Pollution Bulletin* **21**, 481

Davis, M. B. & Ford, M. S. (1982) Sediment focusing in Mirror Lake, New Hampshire. *Limnology and Oceanography* **27**, 137–50

Davison, W. (1993) Iron and manganese in lakes. *Earth-Science Reviews* **34**, 119-163

DEFRA (2002) Soil Guideline Values for Lead Contamination. Environmental Agency, Bristol.

De Vos, W., Batista, M.J., Demetriades, A., Duris, M., Lexa, J., Lis, J., Marsina, K. & O'Connor, P., 2005. Metallogenic mineral provinces and world class ore deposits in Europe. In: Salminen, R. (Chief-editor), Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson S.Å., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A. & Tarvainen, T., FOREGS Geochemical Atlas of Europe, Part 1and 2 Geological Survey of Finland, Espoo: 43-49

De Voto, E., Yorkel, R.A. (1994) Aluminum Speciation and Toxicokinetics. *Environmental Health Perspectives* **102,** 940-951

Dearing, J.A., Bird, P.M., Dann, R.J.L. and Benjamin, S.F. (1997) Secondary ferromagnetic minerals in Welsh soils: a comparison of mineral magnetic detection methods and implications for mineral formations. *Geophysical Journal International* **130**, 727-736

Dearing, J.A., Dann, R.J.L., Hay, K.L., Lees, J.A., Loveland, P.J., Maher, B.A. and O'Grady, K. (1996) Frequency-dependant susceptibility measurements of environmental materials. *Geophysics Journal International* **124**, 228-240

Dearing, J.A., Hannam, J.A., Anderson, A.S. and Wellington, E.M.H. (2001) Magnetic, geochemical and DNA properties of highly magnetic soils in England. *Geophysics Journal International* **144**, 183-196

Deely, J.M. and Ferguson, J.E. (1994) Heavy metal and organic matter concentrations and distributions in dated sediments of a small estuary adjacent to a small urban area. *The Science of the Total Environment* **153**, 97-111

Devitre, R., Belzile, N., Tessier, A., (1991) Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. *Limnology and Oceanography* **36,** 1480-1485

Dockery, D.W., Pope, C.A., Xu, X. *et al.* (1993) An association between air pollution and mortality in six U.S. cities. New England Journal of Medicine **329**, 1753–1759.

Dockery, D.W. (2001) Epidemiologic evidence of cardiovascular effects of particulate air pollution. *Environ Health Perspect*ives **109,** 483–486

Edgar, P.J., Hursthouse, A.S., Matthews, J.E. and Davies, I.M. (2003) An investigation of geochemical factors controlling the distribution of PCBs in intertidal sediments at a contamination hot spot, the Clyde Estuary, UK. *Applied Geochemistry* **18**, 327-338

Eggleton, J., Thomas, K.V. (2004) A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. *Environment International* **30**, 973-980

Eisenreich, S. J., Capel, P. D., Robbins, J. A. & Bourbonniere, R. (1998) Accumulation and diagenesis of chlorinated hydrocarbons in lacustrine sediments. *Environmental Science and Technology* **23**, 1116–26

Eskenazi, B., Mocarelli, P., Warner, M., Samuels, S., Vercellini, P., Olive, D., Needham, L., Patterson, D., and Brambilla, P. (2000). Seveso Women's Health Study: a study of the effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin on reproductive health. *Chemosphere* **40**, 913-1288

Evans, G., Howarth, R.J. and Nombela, M.A. (2003) Metals in sediments of Ensenada de San Simon (inner Ria de Vigo), Galicia, NW Spain. *Applied Geochemistry* **18**, 973-996

Farina, M., Esquivel, D.M.S. and Lins de Barros, H.G.P. (1990) Magnetic iron-sulphur crystals from a magnetotactic microorganism. *Nature* **343**, 256-258

Finkelstein, Y., Markowitz, M. and Rosen, J. (1998) Low-level lead-induced neurotoxicity in children: an update on central nervous system effects. *Brain Research Reviews* **27** 168–176.

Finney, B.P. and Huh, C.A. (1989) History of metal pollution in the Southern Californian Bight: an update. *Environmental Science and Technology* **23,** 294-303

Fischer, A.B. (1987) Mutagenic effects of cadmium alone and in combination with antimutagenic selenite. Proc. 6th Int. Conf. on Heavy Metals in the Environment, New Orleans, Vol. 2.CEP Consultants Ltd, Edinburgh. 112-114

Flanders, P.J. (1994) Collection, measurement and analysis of of airborne magnetic particulates from pollution in the environment. *Journal of Applied Physics* **75**, 5931-5936

Forster, T.H., Evans, M.E. and Heller, F. (1994) The frequency-dependence of low field susceptibility in loess sediments. *Geophysics Journal International* **118**, 636-642

Forstner, U. (1977) Metal concentrations in Recent lacustrine sediments. *Arch. Hydrobiologica.* **80**, 172-191

Forstner, U. and Salomons, W. (1980) Trace metal analysis on polluted sediments. Part 2. Evaluation of environmental impact. *Environmental Technology Letters* **1**, 506-517

Forstner, U. and Muller, G. (1981) Concentrations of heavy metal sand polycyclic aromatic hydrocarbons in river sediments: geochemical background, man's influence and environmental impact. *GeoJournal* **5.5** 417-432

Fox, W.M., Connor, L., Copplestone, D., Johnson, M.S. and Leah, R.T. (2001) The organochlorine history of the Mersey estuary, UK, revealed by analysis of sediment cores from saltmarshes. *Marine Environmental Research* **51**, 213-227

Fox, W.M., Johnson, M.S., Jones, S.R., Leah, R.T. and Copplestone, D. (1999) The use of sediment cores from stable and developing saltmarshes to reconstruct historical contamination profiles in the Mersey Estuary, UK. *Marine Environmental Research* **47**, 311-329

Fralick. P.W. and Kronberg, B.I. (1997) Geochemical discrimination of clastic sedimentary rock sources. *Sedimentary Geology* **113**, 111–124

Friberg L., Elinder C.G., Kjellstroem T. and Nordberg G.F. (eds.) (1986a).Cadmium and Health: A Toxicological and Epidemiological Appraisal. Volume 11, Effects and Response. CRC Press, Boca Raton, Florida.

Friberg L., Kjellstroem T. and Nordberg G.F. In: Friberg L, Nordberg GF And Vonk VB (eds.). (1986[b]).Handbook on the Toxicology of Metals, Volume 11. Elsevier, Amsterdam. New York. Oxford. 130-184.

Ganrot, P.O. (1986) Metabolism and possible health effects of aluminium. *Environmental Health Perspectives,* **65**, 363-441

Garcia-Perez, J., Pollan, M., Boldo, E. *et al.* (2009) Mortality due to lung, laryngeal and bladder cancer in towns lying in the vicinity of combustion installations. *Science of the Total Environment* **407,** 2593-602

George, N. (1997) Liverpool Bay Natural area; a nature conservation profile. NA 117, English Nature

Georgeaud, V.M., Rochette, P., Ambrosi, J.P., Vandamme, D., Williamson, D. (1997) Relationship between heavy metals and magnetic properties in a large polluted catchment: The Etang de Berre (South of France). *Phys. Chem. Earth* **22,** 211-214.

Gevao, B., Hamilton-Taylor, J., Murdoch, C., Jones, K.C., Kelly, M. and Tabner, B.J. (1997) Depositional time trends and remobilisation of PCBs in lake sediments. *Environmental Science and Technology* **31**, 3274-3280

Gevao, B., Hamilton-Taylor, J., Jones, K.C. (1998) Polychlorinated biphenyl and polycyclic aromatic hydrocarbon deposition to and exchange at the air-water interface of Esthwaite water, a small lake in Cumbria, UK. *Environmental Pollution* **102,** 63-75

Gevao, B., Hamilton-Taylor, J., Jones, K.C. (2000) Towards a complete mass balance and model for PCBs and PAHs in a small rural lake, Cumbria UK. *Limnology and Oceanography* **45,** 881-894

Giblin, A.E., Bourg, A., Valiela, I. *et al.* (1980) Uptake and losses of heavy metals in sewage sludge by a New England salt-marsh. *American Journal of Botany* **67**, 1059-1068

Giblin, A.E., Valiela, I., Teal, J.M. (1983) The fate of metals introduced into a New England salt-marsh. *Water Air and Soil Pollution* **20**, 81-98

Giblin, A.E. and Howarth, R.W. (1984) Porewater evidence for a dynamic sedimentary iron cycle in saltmarshes. *Limnology and Oceanography* **29**, 47-63

Giblin, A.E., Luther, G.W., Valiela, I. (1986) Trace-metal solubility in salt-marsh sediments contaminated with sewage-sludge. *Estuarine Coastal and Shelf Science* **23,** 477-498

Gil, K.I., Kim, L.H., Cho, G.C., Yoon, J. (2010) Evaluation of sediment contamination and effectiveness of dredging in mid to lower Han river. *Soil Air and Water Pollution* **206** 263-272

Gil, O. and Vale, C. (2001) Evidence of polychlorinated biphenyls dechlorination in the sediments of the Sado estuary, Portugal. *Marine Pollution Bulletin* **42**, 453-461

Gobeil, C., Silverberg, N. and Silverberg, N. (1981) Factors influencing particulate organic matter geochemistry in the St Lawrence estuary turbidity maxiumun. *Marine Chemistry* **10,** 123-140.

Gocht, T., Moldenhauer, K.M., Puttmann, W. (2001) Historical record of polycyclic aromatic hydrocarbons (PAH) and heavy metals in floodplain sediments from the Rhine River (Hessisches Ried, Germany). *Applied Geochemistry* **16.** 1707-1721

Gonsiorczyk, T., Casper, P., Koschel, R. (1998) Phosphorus-binding forms in the sediment of an oligotrophic and an eutrophic hardwater lake of the Baltic lake district (Germany). *Water Science and Technology* **37,** 51-58

Goodarzi, F., Reyes, J., Schulz, J. *et al.* (2006) Parameters influencing the variation in mercury emissions from an Alberta power plant burning high inertinite coal over thirty-eight weeks period. *International Journal of Coal Geology* **65,** 26-34

Grayson, R.P., Plater, A.J. (2009) A lake sediment record of Pb mining from Ullswater, English Lake District, UK. *Journal of Paleolimnology* **42,** 183-197

Guallar, E., Sanz-Gallardo, M.I., Van't Veer, P. *et al.* (2002) Mercury, fish oils, and the risk of myocardial infarction. *New England Journal of Medicine* **347,** 1747-1754

Gunn, J.M. (ed) (1995) Restoration and recovery of an industrial region. New York: springer-verlag

Guo, H., Lee, S.C., Ho, K.F. *et al.* (2003) Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmospheric Environment* **37,** 5307-5317

Gupta, P., Banerjee, D.K., Bhargava, S.K. *et al.* (1993) Prevalence of impared lung function in rubber manufacturing factory workers exposed to benzo(a)pyrene and respirable particulate matter. *Indoor Environment* **2,** 26-31

Gustafsson, O., Bucheli, T.D., Kukulska, Z., Andersson, M., Largeau, C. and Rouzard J.N. *et al.*, (2001) Evaluation of a protocol for the quantification of black carbon in sediments. *Global Biogeochemical Cycles* **15,** 881–890

Habs, M., Schmahl, D., Misfeld, J. (1980) Local carcinogenicity of some environmentally relevant polycyclic aromatic hydrocarbons after lifelong topical application to mouse skin. *Arch Geschwulstforsch* **50,** 266-274

HamiltonTaylor, J., Davison, W., Morfett, K. (1996) A laboratory study of the biogeochemical cycling of Fe, Mn, Zn and Cu across the sediment-water interface of a productive lake. *Aquatic Sciences* **58,** 191-209

Hammond, E.D., Selikoff, I.J., Lawther, P.O. *et al.* (1976). Inhalation of b[a]p and cancer in man. *Ann Ny Acad Sci* **271**:116-124

Handley, J.F. and Wood, R.W.S. (1999) The consequences of landscape change; principles and practice; problems and opportunity. *Ecology & Landscape Development: A History of the Mersey Basin* Liverpool University Press 2004

Hansen, J. (2000) Elevated risk for male breast cancer after occupational exposure to gasoline and vehicular combustion products. *American Journal of Industrial Medicine* **37,** 349-352

Hansen, L.D., Silberman, D. and Fisher, G.L. (1981) Crystalline componets of stack-collected, size-fractioned coal fly-ash. *Environmental Science and Technology* **15**, 1057-1062

Hardie, D. W. (1950) A history if the chemical industry at Widnes. Kynoch Press Birmingham.

Harikumar, P. S., Nasir, U. P., Mujeebu Rahman, M. P. (2009) Distribution of heavy metals in the core sediments of a tropical wetland system.. *International Journal of Environmental Science and Technology* **6,** 225-232

Harland, B.J., Taylor, D. and Wither, A. (2000) The distribution of mercury and other trace metals in the sediments of the Mersey estuary over 25 years 1974-1998. *The Science of the Total Environment* **253**, 45-62

Hartnett, M., Berry, A. (2010) Transport of lead in the Mersey Estuary: The development of a novel approach to deriving partition coefficients. *Advances in Engineering Software* **41,** 84-91

Harvey, G.R. (1980) A study of the chemistry of iodine and bromine in marine sediments. *Marine Chemistry* **8,** 327–332

Hay, K.L., Dearing, J.A., Baban, S.M.J. and Loveland, P. (1997) A preliminary attempt to identify atmospherically-derived pollution particles in English topsoils from magnetic susceptibility measurements. *Phys. Chem.* Earth **22**, 207-210.

Hayhurst, D.T., Nastro, A., Aiello, R. *et al.* (1998) Effect of hydroxide on growth-rate and morphology in silicalite synthesis. *Zeolites* **8**, 416-422

Heinrich U. (1988) Carcinogenicity of cadmium - Overview of experimental and epidemiological results and their influence on recommendations for maximum concentrations in the occupational area. In: Hutzinger O. and Safe S.H. (eds.) Environmental Toxins, Volume 2, Cadmium. (Vol. eds.: Stoeppler M. and Piscator M.). Springer, Berlin-Heidelberg. New York-London-Paris-Tokyo. 13-15. Kontamination des Wassers in Bereich von Abfallhalden durch Wiley, New York. 35-41.

Hellström L., Elinder C.G., Dahlberg B. (2001) Cadmium exposure and end-stage renal disease. *American Journal of Kidney Disease* **38,** 1001-1008

Hilton, J., Lishman, J.P., Allen, P.V. (1986) The dominant processes of sediment distribution and focusing in a small, eutrophic, monomictic lake. *Limnology and Oceanography* **31**, 125-133

Hines, M.E., Lyons, W.M., Armstrong, P.B., Orem, W.H., Spencer, M.J., Gaudette, H.E. and Jones, G.E. (1984) Seasonal metal remobilisation in the sediments of the Great Bay, New Hampshire. *Marine Chemistry* **15**, 173-184

Hirst, J.M., Aston, S.R. (1983) Behavior of Copper, Zinc, Iron and Manganese During Experimental Resuspension and Reoxidation of Polluted Anoxic Sediments. *Estuarine Coastal and Shelf Science* **16,** 549-558

Hjorth, T. (2004) Effects of freeze-drying on partitioning patterns of major elements and trace metals in lake sediments. *Analytica Chimica Acta* **526,** 95

Holden, A. (1981) Organochlorines – an overview. *Marine Pollution Bulletin* **12**, 110-115

Howard, V. (1997) Synergistic effects of chemical mixtures – can we rely on traditional toxicology? *The Ecologist* **27,** 5

Hudson-Edwards, K.A., Macklin, M.G., Curtis, C.D. and Vaughan, D. (1996) Mineralogical forms, processes of formation and distribution of Pb, Zn, Cd, and Cu in the Tyne catchment basin, Northern Pennines, North East England. *Environmental Science and Technology* **30,** 72-80

Huggins, F., Goodarzi, F. (2009) Environmental assessment of elements and polyaromatic hydrocarbons emitted from a Canadian coal-fired power plant. *International Journal of Coal Geology* **77,** 282-288

Hughes S.H (1999) The geochemical and mineralogical record of historical miningwithin estuarine sediments in the upper reaches of the Fal estuary, Cornwall UK. *Special Publication International Association of Sedmimentology* **28**, 161-168

Huntley, S.L., Bonnevie, N.L. and Wenning, R.J. (1995) Polycyclic aromatic hydrocarbon and petroleum hydrocarbon contamination in sediment from the Newark Bay estuary, New Jersey. *Archives of Environmental Contamination and Technology* **28,** 93-107

Hursthouse, A.S., Matthews, J.M., Figures, J.E., Iqbal-Zahid, P., Davies, I.M. and Vaughan, D.W. (2003) Chromium in intertidal sediments of the Clyde, UK: Potential for remobilisation and bioaccumulation. *Environmental Geochemistry and Health* **25**, 171-203

Hussey, R. M. (1990) Health in the Mersey basin: an epidemiological study of health and pollution. University of Liverpool, Department of Public Health

Hutchinson, S.M. (1993) The magnetic record of particulate pollution in a saltmarsh, Dee estuary, UK. *The Holocene* **34**, 342-350

Hutchinson, S.M., Rothwell J.J. (2008) Mobilisation of sediment-associated metals from historical Pb working sites on the River Sheaf, Sheffield, UK. *Environmental Pollution* **155,** 61-71

Hylander, L.D., Meili, M., Oliveira, L.J., de Castro e Silva, E. *et al.* (2000) Relationship of mercury with aluminum, iron and manganese oxy-hydroxides in sediments from the Alto Pantanal, Brazil. *Science of the Total Environment* **260,** 97-107

Ishinishi, N., Kodama, Y. Nobutomo, K. Inamasu, T., Kunitake, E., Suenaga, Y. (1977) Outbreak of chronic arsenic poisoning among retired workers from an arsenic mine in Japan. *Environmental Health Perspectives* **19**, 121-125

Jacobson, J.L., Jacobson, S.W. (1996a.) Dose-response in perinatal exposure to polychlorinated biphenyls (PCBs): The Michigan and North Carolina cohort studies. *Toxicology and Industrial Health,* **12**, 435-445

Jacobson J.L., Jacobson S.W. (1996b.) Intellectual impairment in children exposed to polychlorinated biphenyls *in utero*. *New England Journal Of Medicine*, **335**, 783-789

Jaffe, K.M., Shurtleff, D.B., Robertson, W.O. (1983) Survival after acute mercury-vapor poisoning - role of intensive supportive care. *American Journal of Diseases of Children* **137,** 749-751

Järup L., Hellström L., Alfvén T. (2000) Low level cadmium exposure and early kidney damage – the OSCAR study. *Occupational Environmental Medicine* **57**, 668-672.

Jensen, S. (1966) Report of a new chemical hazard. *New Scientist* **32**, 612

Jones, B. and Turki, A. (1997) Distribution and speciation of heavy metals in surficial sediments from the Tees estuary, north-east England. *Marine Pollution Bulletin* **34**, 768-779

Kannan, N., Tanabe, S., Okamoto, T., Tatsukawa, R. and Phillips, D.J.H. (1989a) Polychlorinated biphenyls (PCBs) in sediments in Hong Kong: a congener-specific approach to the study of coplanar PCBs in aquatic ecosystems. *Environmental Pollution* **62**, 223-235

Kannan, N., Tanabe, S., Ono, M. and Tatsukawa, R. (1989b) Critical evaluation of polychlorinated biphenyl toxicity in terrestrial and marine mammals: Increasing impact of non-*ortho* coplanar polychlorinated biphenyls from land to ocean. *Archives of Environmental Contamination and Toxicology* **18**, 706-727.

Kannan, N., Tanabe, S., Tatsukawa, R. and Phillips, D.J.H. (1989c) Persistancy of highly coplanar PCBs in aquatic ecosystems: uptake and release kinetics of coplanar PCBs in green-lipped mussels (*Perna viridis* Linneaus). *Environmental Pollution* **55**, 65-76

Kapicka, A., Petrovsky, E., Ustjak, S. *et al.* (1999) Proxy mapping of fly-ash pollution of soils around a coal-burning power plant: a case study in the Czech Republic. *Journal of Geochemical Exploration* **66**, 291-297

Karlin, R. and Levei, S. (1983) Diagenesis of magnetic minerals in recent hemipelagic sediments. *Nature* **303**, 327-330

Karlin, R., Lyle, M. and Heath, G.R. (1987) Authigenic magnetite formation in suboxic marine sediments. *Nature* **326**, 490-493.

Kabata-Pendias, A., Mukherjee, A. (2007) Trace Elements from Soil to Human [electronic book] / by.Heidelberg : Springer-Verlag Berlin Heidelberg,

Kazantzis, G. (1987). The mutagenic and carcinogenic effect of cadmium, an update. *Journal of Toxicological and Environmental Chemistry.* **15**, 83-100.

Kerner, M. and Willmann, K. (1992) Remobilisation events involving Cd and Zn from intertidal flat sediments in the Elbe estuary during the tidal cycle. *Estuarine Coastal and Shelf Science* **35**, 371-393

King, A.J., Readman, J.W., Zhou, J.L. (2007) Behaviour of polycyclic aromatic hydrocarbons in dissolved, colloidal, and particulate phases in sedimentary cores. *International Journal of Environmental Analytical Chemistry* **87**, 211-225

Klaassen C., Watkins B. (1999) Casarett and Doull's Toxicology: The basic science of poisons. Companion Handbook, Fifth Edition. The McGraw-Hill Companies..

Klanova, J., Matykiewiczova, N., Macka, Z. *et al.* (2008) Persistent organic pollutants in soils and sediments from James ROSS Island, Antarctica. *Environmental Pollution* **152**, 416-423

Klein, C.B. (1996.) Carcinogenicity and genotoxicity of chromium. In Chang l.w. (ed) *Toxicology of Metals*, CRC Press, Boca Raton Florida, 205-219.

Ko, F.C. and Baker, J.E. (1995) Partitioning of hydrophobic organic contaminants to resuspended sediments and plankton in the mesohaline Chesapeake Bay. *Marine Chemistry* **49**, 171-188

Ko, F.C., Sanford, L.P. and Baker, J.E. (2003) Internal recycling of particle reactive organic chemicals in the Chesapeake Bay water column. *Marine Chemistry* **81**, 163-176

Kolak, J.J., Long, D.T., Kerfoot, W.C. *et al.(*1999) Nearshore versus offshore copper loading in Lake Superior sediments: Implications for transport and cycling. *Journal of Great Lakes Research* **25,** 611-624

Koostka, J.E. and Nealson, K.H. (1995) Dissolution and reduction of magnetite by bacteria. *Environmental Science and Technology* **29**, 2535-2540.

Koppe J.G., De Boer, P. (2001) Immunotoxicity by dioxins and PCB's in the perinatal period. Endocrine Disrupters. *Environmental Science and Technology Library* **18**, 69-79

Koppe J.G., Ten Tusscher G., De Boer, P. (2000) Background exposure to dioxins and PCB's in Europe and the resulting health effects. Health Impacts of Waste Management Policies. Environmental Science and Technology Library 16, 135-154

Kortenkamp, A. (2007) Ten years of mixing cocktails: a review of combination effects of endocrine-disrupting chemicals. *Environmental Health Perspectives* **115 Suppl 1,** 98

Kortenkamp, A., Faust, M., Scholze, M. *et al.* (2007) Low-level exposure to multiple chemicals: reason for human health concerns? *Environmental Health Perspectives* **115 Suppl 1,** 106-14

Kraepiel, A.M.L., Chiffoleau, J.F., Martin, J.M., *et al.* (1997) Geochemistry of trace metals in the Gironde estuary. *Geochimica et Cosmochimica Acta* **61,** 1421-1436

Krivtsov, V., Howarth, M.J., Jones, S.E. *et al.*(2008) Monitoring and modelling of the Irish Sea and Liverpool Bay: An overview and an SPM case study: *Ecological Modelling* **212**, 37-52

Krongborg, O., Fenger, C., Olsen, J., Jorgensen, O.D., Sondergaard, O. (1996) Randomised study of screening for colorectal cancer with faecal–occult–blood test. *Lancet* **348**, 1467–1471

Kuo, C.Y., Cheng, Y.W., Chen, C.Y., *et al.* (1998) Correlation between the amounts of polycyclic aromatic hydrocarbons and mutagenicity of airborne particulate samples from Taichung city, Taiwan. *Environmental Research* **78.** 43-49

Lagervist, B.J. and Zetterlund, B. (1994) Assessment of exposure to arsenic amongst smelter workers: a five year follow-up. *American Journal of Industrial Medicine* **25**, 477-488

Lam, M.H.W., Tjia, A.Y.W., Chan, C.C., Chan, W.P. and Lee, W.S. (1997) Speciation study of chromium, copper and nickel in coastal estuarine sediments polluted by domestic and industrial effluents. *Marine Pollution Bulletin* **34**, 949-959

Lander, J.J., Stanley, R.J., Sumner, H.W., Boswell, D.C., Aach, R.D. (1975) Angiosarcoma of the liver associated with Fowler's solution (potassium arsenite). *Gastroenterology* **68**, 1582-1586

Landrigan, P.J. (1981) Arsenic – state of the art. *American Journal of Industrial Medicine* **2,** 5-14

Lane, A. (2004) Bathymetric evolution of the Mersey Estuary, UK, 1906–1997: causes and effects. *Estuarine Coastal and Shelf Science.* **59,** 249–263

Lane, A., Prandle, D. (2006) Random-walk particle modelling for estimating bathymetric evolution of an estuary. *Estuarine Coastal and Shelf Science* **68,** 175-187

Lang, L. (1995) Strange Brew: assessing risk of chemical mixtures. *Environmental Health Perspectives* **103,** 142-145

Lansdown, R. (1986) Lead, intelligence attainment and behavior. In: Lansdown R. and Yule W. (eds.) The Lead Debate. Croom Helm, London-Sydney. 235-270.

Langston, W.J. (1986) Metals in sediments and benthic organisms in the Mersey estuary. *Estuarine Coastal and Shelf Science* **23,** 239-261

Lara, R. and Ernst, W. (1990) Sorption of polychlorinated biphenyls on marine sediments. I. The role of the organic carbon content. *Environmental Technology* **11,** 83-92

Larsson, P. and Sodergren, A. (1987) Transport of polychlorinated biphenyls (PCBs) in freshwater mesocosms from sediment to water and air. *Soil Air and Water Pollution* **36,** 33-46

Laslett, R.E (1995) Concentrations of Dissolved and Suspended Particulate Cd, Cu, Mn, Ni, Pb And Zn in Surface Waters Around the Coasts of England and Wales and in Adjacent Seas. *Estuarine Coastal and Shelf Science* **40,** 67-85

Latimer, J.S. and Quinn, J.G. (1996) Historical trends and current inputs of hydrophobic organic compounds in an urban estuary: the sedimentary record. *Environmental Science and Technology* **30,** 623-633

Latimer, J.S., Davis, W.R., Keith, D.J. (1999) Mobilization of PAHS and PCBs from in-place contaminated marine resuspension events. *Estuarine Coastal and Shelf Science* **49,** 577-595

Lavoie, E.J., Amin, S., Hecht, S.S. *et al.* (1982) Tumor initiating activity of dihydrodiols of benzo(b)fluoranthene, benzo(j)fluoranthene and benzo(k)fluoranthene. *Carcinogenesis* **3,** 49-52

Law, R.J. (1981) Hydrocarbon concentrations in water and sediments from UK marine waters, determined by fluorescence spectroscopy. *Marine Pollution Bulletin* **12,** 153-157

Law, R.L., Allchin, C.R. and Dixon, A.G. (1991) Polychlorinated biphenyls in sediments downstream of a contaminated industrial site in North Wales. *Marine Pollution Bulletin* **22,** 492-493

Law, R. J., Biscaya, J.L. Polycyclic aromatic-hydrocarbons (PAH) - problems and progress in sampling, analysis and interpretation. *Marine Pollution Bulletin* **29,** 235-241

Leah, R.T., Ma, Z.Y., Evans, S.J. *et al.* Mercury in the stomach contents of dab (limanda-limanda) from the north-east Irish sea and Mersey estuary. *Environmental Pollution* **72,** 117-126

Lee, P.K., Baillif, P., Touray, J.C. (1997) Geochemical behaviour and relative mobility of metals (Mn, Cd, Zn and Pb) in recent sediments of a retention pond along the A-71 motorway in Sologne, France. *Environmental Geology* **32,** 142-152

Lee, S.V., Cundy, A.B. (2001) Heavy metal contamination and mixing processes in sediments from the Humber Estuary, Eastern England. *Estuarine Coastal and Shelf Science* **53,** 619-636

Lee B.E., Ha E.H., Park H.S., Kim Y.J., Hong Y.C., Kim H., Lee J.T. (2003) Exposure to air pollution during different gestational phases contributes to risks of low birth weight. *Human Reproduction* **18,** 638-643

Lee, K.T., Tanabe, S. and Koh, C.H. (2001) Contamination of polychlorinated biphenyls (PCBs) in the sediments from the Kyeonggi bay and the nearby areas, Korea. *Marine Pollution Bulletin* **42**, 273-279

Lehman, J.T. (1975) Reconstructing rate of accumulation of lake sediment - effect of sediment focusing. *Quaternary Research* **5,** 541-550

Lei, L., Khodadoust, A.P., Suidan, M.T. *et al.* (2005) Biodegradation of sediment-bound PAHs in field contaminated sediment. *Water Research* **39,** 349-361

Levin, W., Chang, R.L., Wood, A.W. *et al.* (1984) High stereoselectivity among the optical isomers of the diastereomeric bay-region diol-epoxides of benz(a)anthracene in the expression of tumorigenic activity in murine tumor models. *Cancer Research* **44,** 929-933

Lewis, J.P and Trail, A. (1999) Statistics Explained Addison-Wesley Longman Ltd, Harlow

Lick, W. (1986) Modelling the transport of fine-grained sediments in aquatic systems. *Science of the Total Environment* **55,** 219-228

Liszewski, M.J., Rosentreter, J.J., Miller, K.E., *et al.* (2000) Chemical and physical properties affecting strontium distribution coefficients of surficial-sediment samples at the Idaho. National Engineering and Environmental Laboratory, Idaho *Environmental Geology* **39,** 411-426

Liu, M., Baugh, P.J., Hutchinson, S.M. *et al.* (2000) Historical record and sources of polycyclic aromatic hydrocarbons in core sediments from the Yangtze Estuary, China. *Environmental Pollution* **110,** 357-365

Lloyd, J.W. (1971) Long-term mortality study of steelworkers: v. respiratory cancer in coke plant workers. *Journal of Occupational Medicine* **13**, 53-68

Lockhart, W.L., Macdonald, R.W., Outridge, P.M., *et al.* (2000) Tests of the fidelity of lake sediment core records of mercury deposition to known histories of mercury contamination. *Science of the Total Environment* **260,** 171-180

Lohse, J. (1991) Distribution of organochlorine pollutants in North Sea sediments. *Water Science and Technology* **24,** 107-113

Lopez-Sanchez, J.F., Rubio, R., Samitier, C. and Rauret, G. (1996) Trace metal portioning in marine sediments and sludges deposited off the coast of Barcelona (Spain). *Water Research.* **30**, 153-159

Loring, D.H. and Rantala, R.T.T. (1992) Manual for the geochemical analyses of marine sediments and particulate matter. *Earth Science Reviews* **32**, 235-283

Lu, X., Johnson, W.K., Wong, C.S. (1986) Seasonal replenishment of mercury in a coastal fjord by its intermittent anoxicity. *Marine Pollution Bulletin* **17**, 263-267

Lu, X.Q., Werner, I., Young, T.M. (2005) Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay. *Environment International* **31**, 593-602

Luoma, S.N., Bryan, G.W. (1981) A statistical assessment of the form of trace-metals in oxidized estuarine sediments employing chemical extractants. *Science of the Total Environment* **17**, 165-196

Luomas, N. and Jenne, E.A. (1977) The availability of sediment bound cobalt, silver and zinc to a deposit-feeding clam. In *Biological Imphcations of Metals in the Environment (ed.* H. Drucker andR. E. Wildung) pp. 2 13-230. ERDA Symp. Ser. No. 42; Energy Research and Development Administration.

Luther, G.W., Church, T.M. (1988) Seasonal cycling of sulfur and iron in porewaters of a Delaware salt-marsh. *Marine Chemistry* **23**, 295-309

Ma, F.K., Jiang, C.B., William, B.R. *et al.*(2009) Modelling sediment transport processes in macro-tidal estuary. *Science In China Series E-Technological Sciences* **52**, 3368-3375

MacDonald, D.D., Ingersoll, C.G., Berger, T.A. (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology* **39**, 20-31

Maher, B.A. and Taylor, R.M. (1988) Formation of ultrafine-grained magnetite in soils. *Nature* **336**, 368-370

Maher, B.A. and Thompson R. (1999) Quaternary climates, environments and magnetism. edited by Barbara A. Maher and Roy Thompson. Cambridge University Press

Maher, B.A. (1988) Magnetic-properties of some synthetic sub-micron magnetites. *Geophysical Journal-Oxford* **94**, 83-96

Masuda, Y. (1985) Health status of Japanese and Taiwanese after exposure to contaminated rice oil. *Environmental Health Perspectives* **60**, 321-325

Martin, M., Richardson, B.J. and Lam, P.S.K. (2003) Harmonisation of polychlorinated biphenyl (PCB) analyses for ecotoxicological interpretations of southeast Asian environmental media: what's the problem? *Marine Pollution Bulletin* **46**, 159-170

Martino, M., Turner, A., Nimmo, M. and Millward, G.E. (2002) Resuspension, reactivity and recycling of trace metals in the Mersey estuary, U.K. *Marine Chemistry* **77**, 171-186

Martino, M., Turner, A., Nimmo, M. (2004) Distribution, speciation and particle-water interactions of nickel in the Mersey Estuary, UK. *Marine Chemistry* **88**, 161-177

Maynard R.L. and Howard C.V. (1999) Particulate Matter Properties and Effects on Health. BIOS Scientific Publishers Ltd

Mazumdar, S., Redmond, C.K., Sollecito, W, *et al.* (1975).An epidemiological study of exposure to coal tar pitch volatiles among coke oven workers. *J Air Pollut Control Assoc* **25**, 382-389

McCaffrey, R.J. and Thomson, J. (1980) A record of the accumulation of sediment and trace metals in a Conneticut saltmarsh. *Adv. Geophys* **22**, 165-236

McPherson, K., Steel, C.M., Dixon, J.M. (1994) Breast cancer – epidemiology, risk factors, and genetics. *British Medical Journal* **309**, 1003–1007

Menzie, C.A., Potocki, B.B., Santodonato, J. (1992) Exposure to carcinogenic PAHs in the environment . *Environmental Science and Technology* **26,** 1278-1284

Meyers, P.A., Ishiwatari, R. (1993) Lacustrine organic geochemistry - an overview of indicators of organic-matter sources and diagenesis in lake-sediments. *Organic Geochemistry* **20,** 867-900

Michelutti, N., Laing, T.E., Smol, J.P.(2001) Diatom assessment of past environmental changes in lakes located near the noril'sk (siberia) smelters. *Water Air and Soil Pollution* **125,** 231-241

Millington, R. (1947) Guide to Speke Hall Liverpool: Liverpool printing and stationary co

Mirlean, N., Andrus, V.E., Baisch, P. (2003) Mercury pollution sources in sediments of Patos Lagoon Estuary, Southern Brazil. *Marine Pollution Bulletin* **46,** 331-334

Morillo, J., Usero, J. and Gracia, I. (2004) Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere* **55**, 431-442

Morin, G. & Calas, G., (2006) Arsenic in soils, mine tailings, and former industrial sites. *Elements* **2**, 97-101

Morris, R.J., Law, R.J., Allchin, C.R., Kelly, C.A. and Fileman, C.F. (1989) Metals and organochlorines in dolphins and porpoises of Cardigan Bay, West Wales. *Marine Pollution Bulletin* **20**, 512-523

Morris, W.A., Versteeg, J.K., Marvin, C.H. *et al.* (1994) Preliminary comparisons between magnetic-susceptibility and polycyclic aromatic hydrocarbon content in sediments from Hamilton harbor, western lake Ontario. *Science of the Total Environment* **152,** 153-160

Mudroch, A., Duncan, GA (1986) Distribution of metals in different size fractions of sediment from the Niagara river. *Journal of Great Lakes Research* **12,** 117-126

Muir, D.G.C., Omelchenko, A., Grift, N., Savoie, D., Lockhart, W., Wilkinson, P. and Brunskill, G. (1996) Spatial trends and historical deposition patterns of polychlorinated biphenyls in Canadian midlatitude and Arctic lake sediments. *Environmental Science and Technology* **30**, 3609-3917

Mumford, J.L., Lee, X., Lewtas, J. *et al.* (1993) DNA adducts as biomarkers for assessing exposure to polycyclic aromatic hydrocarbons in tissues from xuan wei women with high exposure to coalcombustion emissions and high lung cancer mortality. *Environmental Health Perspectives* **99**, 83-87

Murray, K.S., Cauvet, D., Lybeer, M., Thomas, J.C. **(1999)** Particle size and chemical control of heavy metals in bed sediment from the Rouge River, southeast Michigan. *Environmental Science & Technology* **33**, 987-992

Muxworthy, A.D. (2001) Effect of grain interactions on the frequency dependence of magnetic susceptibility. *Geophys. J. Int.* **144**, 441-447

Natajaran, M.R., Wu, W.M., Wang, H. Bhatnagar, L. and Jain, M.K. (1998) Dechlorination of spiked PCBs in lake sediments by anaerobic microbial granules. *Water Research* **32**, 3013-3020

Needleman H.L. (1987) Low level lead exposure and children's intelligence: A quantitative and critical review of modern studies. Proc. 6th Int. Conf. on Heavy Metals in the Environment, New Orleans Volume 1.CEP Consultants Ltd., Edinburgh. 1-8.

Nemery, B. (1990) Metal toxicity and the respiratory tract. *European Respiratory Journal* **3**, 202-219

NEPC (1999) Schedule B (1): Guideline on the Investigation Levels for Soil and Groundwater. National Environment Protection (Assessment of Site Contamination) Measure 1999. National Environmental Protection Council Adelaide.

Nienke, G.E., Lee, G.F. (1982) Sorption of zinc by lake-Michigan sediments - implications for zinc water-quality criteria standards. *Water Research* **16**, 1373-1378

Nixon, S.W. (1980) Between coastal marshes and coastal waters – a review of 20 years of speculation and research on the role of salt-marshes in estuarine productivity and water chemistry. *Marine Science* **11**, 437-525

Nriagu, J. O. (1996). A history of global metal pollution. *Science* **272**, 223–224

Nriagu, J.O., Rao, S.S. (1987) Response of lake-sediments to changes in trace-metal emission from the smelters at Sudbury, Ontario. *Environmental Pollution* **44**, 211-218

Nriagu, J.O., Wong, H.K.T. (1986) What fraction of the total metal flux into lakes is retained in the sediments. *Water Air and Soil Pollution* **31**, 1001-1008

Norton, M.G., Jones, P.G.W., Franklin, A. *et al.* (1984) Water-Quality Studies Around the Sewage-Sludge Dumping Site in Liverpool Bay. *Estuarine Coastal and Shelf Science* **19**, 53-67

Norton, M.G., Rowlatt, S.M. and Nunny, R.S. (1984) Sewage sludge dumping and contamination of Liverpool Bay Sediments. *Estuarine Coastal and Shelf Sciences* **19**, 69-87

O'Connor, B.A., (1987) Short and long term changes in estuary capacity. *Journal of the Geological Society (Lond.)* **144**, 187–195.

Oldfield, F. (1990) Magnetic measurements of recent sediments from Big Moose Lake, Adirondack Mountains, NY, USA. *Journal of Paleolimnology* **4**, 93-101

Oldfield, F. (1991) Environmental Magnetism - A Personal Perspective. *Quaternary Science Reviews* **10**, 73-85

Oldfield, F. (1994) Toward the discrimination of fine-grained ferrimagnets by magnetic measurements in lake and near-shore marine sediments. *Journal of Geophysical Research* **99**, 9045-9050

Oldfield, F. and Scoullos, M. (1984) Particulate pollution monitoring in the Elefsis Gulf: the role of mineral magnetic studies. *Marine Pollution Bulletin* **15**, 229-231

Oldfield, F., Yu, L.H. (1994) The influence of particle-size variations on the magnetic-properties of sediments from the north-eastern Irish sea. *Sedimentology* **41**, 1093-1108

Oldfield, F. and Wu, R. (2000) The magnetic properties of recent sediments of Brothers Water, N W England. *Journal of Paleolimnology* **23**, 165-174

Olsen, C.R., Cutshall N.H. and Larsen, I.L. (1982) Pollutant-particle associations and dynamics in coastal marine environments: a review. *Marine Chemistry* **11**, 501 –533.

O'Reilly Weise, S.B., MacLeod, C.L. and Lester, J.N. (1997) A recent history of metal accumulation in the sediments of the Thames estuary, United Kingdom. *Estuaries* **20**, 483-493

O'Reilly Wiese, S.B., Bubb, J.M. and Lester, J.N. (1995) The significance of sediment metal concentrations in two eroding Essex saltmarshes. *Marine Pollution Bulletin* **30**, 190-199

Orson, R.A., Simpson, R.L. and Good, R.E. (1992) A mechanism for the accumulation and retention of heavy metals in tidal freshwater marshes of the upper Delaware River estuary. *Estuarine, Coastal and Shelf Science* **34**, 171-186

Ostrea E.M., Morales V., Ngoumgna E., Prescilla R., Tan E., Hernandez E., Ramirez G.B., Cifra H.L., Manlapaz M.L. (2002) Prevalence of Fetal Exposure to Environmental Toxins as Determined by Meconium Analysis. *Neurotoxicology* **23**, 329-339

Palheiros, I.B., Duarte, A.C., Oliveira, J.P. and Hall, A. (1989) The influence of pH, ionic strength and chloride concentration on the adsorption of cadmium by sediment. *Water Science and Technology* **21**, 1873-1876

Paulson, A.J., Curl, H.C., Gendron, J.F. (1994) Partitioning of Cu in estuarine waters .1. Partitioning in a poisoned system. *Marine Chemistry* **45**, 67-80

Perera F., Hemminki K., Jedrychowski W., Whyatt R., Campbell U., Hsu Y.Z., Santella R., Albertini R., O'Neill J.P. (2002) In utero DNA damage from environmental pollution is associated with somatic gene mutation in newborns. *Cancer Epidemiology Biomarkers & Prevention* **11**, 1134-1137

Petersen, W., Wallmann, K., Li, P.L., Schroeder, F. and Knauth, H.D. (1995) Exchange of trace elements at the sediment-water interface during early diagenesis processes. *Marine and Freshwater Research* **46**, 19-26

Pereira, W.E., Hostettler, F.D., Luoma, S.N., *et al.* (1999) Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. *Marine Chemistry* **64**, 99-113

Pierard, C., Budzinski, H. and Garrigues, P. (1996) Grain-size distribution of polychlorinated biphenyls in coastal sediments. *Environmental Science and Technology* **30**, 2776-2783

Plater, A.J. and Appleby, P.G. (2004) Tidal sedimentation in the Tees estuary during the 20th century: radionuclide and magnetic evidence of pollution and sedimentary response. *Estuarine, Coastal and Shelf Science* **60**, 179-192

Plater, A.J., Ridgeway, J., Appleby, P.G., Berry, A. and Wright, M.R. (1998) Historical contaminant fluxes in the Tees estuary, UK: geochemical, magnetic and radionuclide evidence. *Marine Pollution Bulletin* **37**, 343-360

Platt, M.J., Ashton, J. (1991) Health and deprivation in Mersey Region. Observatory Report Series 2.Liverpool Public Health Observatory

Platt, I.S.L., Pfeiffer, E., Petrovic, P. *et al.* (1990). Comparative tumorigenicity of picene and dibenz[a,h]anthracene in the mouse. *Carcinogenesis* **11,** 1721-1726

Platts, M.M. and Anastassiades, E. (1981) Dialysis encephalopathy: precipitating factors and improvement in prognosis. *Clinical Nephrology.* **15**, 223-228

Prats, D., Riuz, F. and Zarzo, D. (1992) Polychlorinated biphenyls and organochlorine pesticides in marine sediments. *Marine Pollution Bulletin* **24**, 441-446

Prartono, T., Wolff, G.A. (1998) Organic geochemistry of lacustrine sediments: a record of the changing trophic status of Rostherne Mere, UK. *Organic Geochemistry* **28,** 729-747

Preston, M.R. and Raymundo, C.C. (1993) The association of linear alkyl benzenes with the bulk properties of sediments from the River Mersey estuary. *Environmental Pollution* **81,** 7-13

Power, A.L., Worsley, A.T., Booth, C.A. *et al.* (2005) The role of urban lake sediments as historical archives of industrial pollution and health linkages: an example from Daresbury pond, north Cheshire, UK. *Environmental Health Risk III* **9,** 363-371

Power, A.L., Worsley, A.T. (2009) Using urban man-made ponds to reconstruct a 150-year history of air pollution in northwest England. *Environmental Geochemistry and Health* **31,** 327-338

Pye, K. (1991). Beach deflation and backshore dune formation following erosion under storm surge conditions: an example from northwest England. *Acta Mech., Suppl.* **2,** 171–181

Pye, K., Blott, S.J. (2008) Decadal-scale variation in dune erosion and accretion rates: An investigation of the significance of changing storm tide frequency and magnitude on the Sefton coast, UK. *Geomorphology* **102**, 652-666

Quinn, M., Babb, P., Brock, A., Kirby, L., Jones. J. (2001) Cancer Trends in England and Wales 1950 – 1999. Office of National Statistics

Rae, J.E. (1997) Trace metals in deposited intertidal sediments. in *Biogeochemistry of intertidal sediments* Edited by Jickells, T.D. and Rae, J.E. Cambridge environmental chemistry series 9. Cambridge University Press. Cambridge.

Rae, J.E. and Allen, J.R.L. (1993) The significance of organic matter degredation in the interpretation of historical pollution trends in depth profiles of estuarine sediment. *Estuaries* **16**, 678-682

Rae, J.E., Aston, S.R. (1981) Mercury in coastal and estuarine sediments of the northeastern Irish sea. *Marine Pollution Bulletin* **12,** 367-371

Ramamoorthy, S., Moore, J.W., George, L. (1985) Partitioning of mercury in the north saskatchewan river. *Chemosphere* **14**, 1455-1468

Ramster, J.W., Hill, H.W. (1969) Current systems in the northern Irish Sea. *Nature* **224**, 59–61

Ratola, N., Lacorte, S., Alves, A. *et al.* (2006) Analysis of polycyclic aromatic hydrocarbons in pine needles by gas chromatography-mass spectrometry - Comparison of different extraction and clean-up procedures. *Journal of Chromatography A* **1114,** 198-204

Rathbun, J.E., Huellmantel, L.L., Tracy, M, *et al.*(1996) Rapid sediment assessment: Indicator analysis and screening analysis approaches . *Journal of Great Lakes Research* **22,** 523-533

Readman, J.W., Preston, M.R., Mantoura, R.F.C., (1986) An integrated technique to quantify sewage, oil and PAH pollution in estuarine and coastal environments. *Marine Pollution Bulletin* **17,** 298-308

Readman, J.W., Mantoura, R.F.C., Rhead, M.M. (1987) A record of polycyclic aromatic hydrocarbon (pah) pollution obtained from accreting sediments of the tamar estuary, uk - evidence for nonequilibrium behavior of PAH. *Science of the Total Environment* **66,** 73-94

Redmond, E., Strobino, B., Cypress, R. (1976). Cancer experience among coke by-product workers. *Ann Ny Acad Sci* **2-7**, 102-115

Reed, D.J. (1995) The response of coastal marshes to sea-level rise - survival or submergence. *Earth Surface Processes and Landforms* **20**, 39-48

Rees, P. (2007) A guide to Merseysides industrial past. The North Western Society for Industrial Archaeology and History, Liverpool Museum, Liverpool.

Reimann, C. & de Caritat P. (1998) Chemical elements in the environment - Factsheets for the geochemist and environmental scientist. Springer-Verlag, Berlin-Heidelberg

Rice, D.C. (1997) Neurotoxicity produced by developmental exposure to PCBs. Mental Retardation and Developmental Disabilities. *Research Reviews* **3**, 223-229

Rice, J.E., Coleman, D.T., Hosted, T.J.J., *et al.* (1985).Identification of mutagenic metabolites of indeno[l,2,3-cd] pyrene formed in vitro with rat liver enzymes. *Cancer Research* **45**, 5421-5425

Ridgeway, J. and Shimmield, G. (2002) Estuaries as repositories of historical contamination and their impact on shelf seas. *Estuarine, Coastal and Shelf Science* **55**, 903-928

Ridgeway, J., Breward, N., Langston, W.J., Lister, R., Rees, J.G. and Rowlatt, S.M. (2003) Distinguishing between natural and anthropogenic sources of metals entering the Irish Sea. *Applied Geochemistry* **18**, 283-309

Rogan, W.J., Gladen, B.C. (1992) Neurotoxicology of PCBs and Related Compounds. *Neurotoxicology,* **13**, 27-35

Rogers, H.R. (2002) Assessment of PAH contamination in estuarine sediments using the equilibrium partitioning-toxic unit approach. *Science of the Total Environment* **290**, 139-155

Rognerud, S., Fjeld, E. (2001) Trace element contamination of norwegian lake sediments. *Ambio* **30,** 11-19

Rosenlund, M., Berglind, N., Pershagen, G.O., *et al.* (2006) Long-Term exposure to urban air pollution and myocardial infarction. *Epidemiology* **17,** 383–390

Rothermich, M.M., Hayes, L.A., Lovley, D.R. (2002) Anaerobic, sulfate-dependent degradation of polycyclic aromatic hydrocarbons in petroleum-contaminated harbor sediment. *Environmental Science & Technology* **36,** 4811-4817

Rothwell, J.J., Dise, N.B., Taylor, K.G. *et al.* (2010) A spatial and seasonal assessment of river water chemistry across North West England. *Science of the Total Environment* **408,** 841-855

Rowens, B., Guerrerobetancourt, D., Gottlieb, C.A., *et al.* (1991) Respiratory-failure and death following acute inhalation of mercury-vapor - a clinical and histologic perspective. *Chest* **99,** 185-190

Rubio, R., Pye, K., Rae, J.E. and Rey, D. (2001) Sedimentological characteristics, heavy metals distribution and magnetic properties in subtidal sediments, Ria de Pontevedra, NW Spain. *Sedimentology* **48**, 1277-1296

Rylander, L., Strömberg, U., and Hagmar, L. (2000) Lowered birth weight among infants born to women with a high intake of fish contaminated with persistent organochlorine compounds. *Chemosphere* **40**, 913-1288

Samman, S., Roberts, D.C.K, (1987) The effect of zinc supplements on plasma zinc and copper levels and the reported symptoms in healthy-volunteers. *Medical Journal of Australia* **146,** 246

Sanei, H., Goodarzi, F. (2006) Relationship between organic matter and mercury in recent lake sediment: The physical-geochemical aspects. *Applied Geochemistry* **21,** 1900-1912

Saper, R.B., Kales, S.N., Paquin, J. *et al.*(2004) Heavy metal content of Ayurvedic herbal medicine products. *Journal of the American Medical Association* **292,** 2868-2873

Schaller, T., Moor, H.C., Wehrli, B. (1997) Sedimentary profiles of Fe, Mn, V, Cr, As and Mo as indicators of benthic redox conditions in Baldeggersee. *Aquatic Sciences* **59,** 345-361

Scoullos, M.J., Olfield, F. and Thompson, R. (1979) Magnetic monitoring of marine particulate pollution in the Elefsis Gulf, Greece. *Marine Pollution Bulletin* **10**, 287-291

Scoullos. M.J. (1986) Trace metal and magnetic studies of sediments in Greek estuaries and enclosed gulfs. *Marine Chemistry* **18**, 249-268

Scrimshaw, M.D. and Lester, J.N. (1996) The occurrence and effects of organic mircopollutants in saltmarsh sediments with reference to the UK Essex coast: a review. *Environmental technology* **17,** 951-964

Scrimshaw, M.D., Bubb, J.P. and Lester, J.N. (1994) Magnitude and distribution of contaminants in saltmarsh sediments of the Essex coast. IV. Organochlorine insecticides and polychlorinated biphenyls. *Science of the Total Environment* **155**, 73-81

Seaton, A., Macnee, W., Donaldson, K., *et al.* (1995) Particulate air-pollution and acute health-effects. *Lancet* **345**, 176-178

Shiller, A.M. & Frilot, D.M., (1996) The geochemistry of gallium relative to aluminum in Californian streams. *Geochimica et Cosmochimica Acta*, **60**, 1323-1328

Schottenfeld, D., Fraumeni, J.F. Jr (eds). (1996) *Cancer Epidemiology and Prevention*. 2nd Edition, New York: Oxford University Press

Simmons, J.E. (1995) Chemical mixtures: Challenge for toxicology and risk assessment. *Toxicology* **105,** 111

Simpson, M.G., Walker, P., Helm, A. *et al.* (2002) Histopathological observations on liver, kidney and gonad of plaice (Pleuronectes platessa) taken from the Mersey estuary. *Marine Environmental Research* **54,** 543-546

Slaga, T.J., Gleason, G.L., Wells, G. (1980) Comparison of the skin tumor-initiating activities of dihydrodiols and diol-epoxides of various polycyclic aromatic hydrocarbons. *Cancer Research* **40**, 1981-1984

Sly, P.G. (1984) Sedimentology and geochemistry of modern sediments in the Kingston basin of lake-Ontario. *Journal of Great Lakes Research* **10,** 358-374

Smedley, P.L., Kinniburgh, D.G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* **17,** 517-568

Snowball, I. and Thomposn, R. (1992) The occurrence of greigite in sediments from Loch Lomond. *Journal of Quaternary Science.* **3**, 121-125

Sokol, R.C., Kwon, O.S., Bethoney, C.M. *et al.* (1994) Reductive dechlorination of polychlorinated-biphenyls in St-Lawrence-river sediments and variations in dechlorination characteristics. *Environmental Science and Technology* **28,** 2054-2064

Sokol, R.C., Bethoney, C.M., Rhee, G.Y. (1995) Effect of PCB concentration on reductive dechlorination and dechlorination potential in natural sediments. *Water Research* **29,** 45-48

Song, Y.F., Jing, X., Fleischmann, S., *et al.* (2002) Comparative study of extraction methods for the determination of PAHs from contaminated soils and sediments. *Chemosphere* **48,** 993-1001

Spencer, K.L., Cundy, A.B., Croudace, I.W. (2003) Heavy metal distribution and early-diagenesis in saltmarsh sediments from the Medway Estuary, Kent, UK. *Estuarine Coastal and Shelf Science* **57,** 43-54

Staples, B., Howse, M.L.P., Mason H. (2003) Land contamination and urinary abnormalities: cause for concern? *Occupational Environmental Medicine*. **60,** 463-467

Stolz, J.F., Chang, S.R. and Kirschvink, J.L. (1986) Magnetotactic bacteria and single-domain magnetite in hemipelagic sediments. *Nature* **321,** 849-851

Stupples, P., Plater, A.J. (2007) Statistical analysis of the temporal and spatial controls on

tidal signal preservation in late Holocene tidal rhythmites, Romney marsh, southeast England. *International Journal of Earth Sciences* **96,** 957-976

Svensson, B.G., Mikoczy, Z., Stromberg, U., Hagmar, L. (1995) Mortality and Cancer Incidence Among Swedish Fishermen with a High Dietary-Intake of Persistent Organochlorine Compounds. *Scandinavian. Journal of Work Environment & Health* **21,** 106-115

Takamatsu, T., Kawashima, M., Koyama, M. (1985) The role of mn-2+-rich hydrous manganese oxide in the accumulation of arsenic in lake-sediments. *Water Research* **19,** 1029-1032

Tanabe, S., Kanna, N., Subramanian, A.N., Watanabe, S. and Tatusakawa, R. (1987) Highly toxic coplanar PCBs: occurance, source, persistency and toxic implications to wildlife and humans. *Environmental Pollution* **47**, 147-163

Tarduno, J.A. (1995) Superparamagnetism and reduction diagenesis in pelagic sediments - enhancement or depletion. *Geophysical Research Letters* **22**, 1337-1340

Taylor, D. (1986) Changes in the distribution patterns of trace-metals in sediments of the mersey estuary in the last decade (1974-83). *Science of the Total Environment* **49,** 257-295

Taylor, S.R., Mclennan, S.M. (1995) The geochemical evolution of the continental crust. *Reviews of Geophysics* **33**, 241-265

Temmerman, S., Govers, G., Wartel, S. *et al.* (2003) Spatial and temporal factors controlling short-term sedimentation in a salt and freshwater tidal marsh, Scheldt estuary, Belgium, SW Netherlands. *Earth Surface Processes and Landforms* **28,** 739-755

ten Tusscher G.W., Steerenberg P.A., van Loveren H., Vos J.G., Von dem Borne A.E.G.K., Westra M., Van der Slikke J.W., Olie K., Pluim H.J., Koppe J.G.(2003) Persistent hematologic and immunologic disturbances in 8-year-old Dutch children associated with perinatal dioxin exposure. *Environmental Health Perspectives* **111,** 1519-1523

Tessier A., Rapin F., and Carignan R. (1985) Trace metals in oxic lakes sediments: Possible adsorption onto iron oxyhydroxides. *Geochimica.et Cosmochimica. Acta.* **49**, 183-194

Thomas, C.G. (1999) Analysis of Bathymetric Surveys of the Mersey Estuary, Report IT 469. HR Wallingford, Wallingford.

Thomas, C.G., Spearman, J.R., Turnbull, M.J. (2002) Historical morphological change in the Mersey Estuary. *Continental Shelf Research* **22**, 1775-1794

Thompson, A., Allen, J.R., Dodoo, D., Hunter, J., Hawkins, S.J. and Wolff, G.A. (1996) Distributions of chlorinated biphenyls in mussels and sediments from Great Britian and the Irish Sea coast. *Marine Pollution Bulletin* **32**, 232-237

Thompson, A., McMorn, P. and Wolff, G.A. (1998) A rapid method for the clean-up of chlorinated biphenyls (CBs) isolated from environmental samples. *Talanta* **45**, 1001-1006

Thompson, R., Bloemendal, J., Dearing, J.A., *et al.* (1980) Environmental applications of magnetic measurements. *Science* **207,** 481-486

Thompson, R. and Oldfield, F. (1986) *Environmental Magnetism.* Allen and Unwin. London

Thomson, E.A., Luoma, S.N., Cain, D.J., Johansson, C. (1980) The effect of sample storage on the extraction of Cu, Fe, Zn, Mn and organic materials from estuarine sediment. *Water Air Soil Pollution* **14,** 215-233

Thorne, L.T. and Nickless, G. (1981) The relation between heavy metals and particle size fractions in Severn estuary (U.K.) intertidal sediments. *Science of the Total Environment* **19,** 207-213

Tibbles, A.J. (1983) Speke hall: a guide to its history and owners. Merseyside county museums, Liverpool

Tomlinson, D. C., Wilson, J, G., Harris, C. R., Jeffery, D. W. (1980). Problems in the assessment of heavy metals levels in estuaries and the formation of a pollution index. *Helgol. Wiss. Meeresunters*, **33,** 566-57

Tomlinson, R. (1997) The Urban Mersey Basin Natural Area. NA 26, English Nature

Tran, T.T., Chowanadisai, W., Crinella, F.M., Chicz-DeMet, A. and Lönnerdal, B.(2002) Effect of High Dietary Manganese Intake of Neonatal Rats on Tissue Mineral Accumulation, Striatal Dopamine Levels, and Neurodevelopmental Status. *NeuroToxicology* **23**, 635–643

Turekian, K.K.. and Wedepohl, K.H. (1961) Distribution of the elements in some major units of the earth's crust. *Geol. Soc. Am. Bull* **72,** 175-192

Turner, A. (2000) Trace metal contamination in sediments from U.K. estuaries: an empirical evaluation of the role of hydrous iron and manganese oxides. *Estuarine, Coastal and Shelf Science* **50**, 355-371.

Turner, A., Millward, G.E., Le Roux, S.M. (2004) Significance of oxides and particulate organic matter in controlling trace metal partitioning in a contaminated estuary. *Marine Chemistry* **88**, 179-192

Tyler, A.O., Millward, G.E., Jones, P.H. and Turner, A. (1994) Polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans in sediments from U.K. estuaries. *Estuarine, Coastal and Shelf Science* **39**, 1-13.

Tylmann, W., Lysek, K., Kinder, M. *et al.* (2011) Regional Pattern of Heavy Metal Content in Lake Sediments in Northeastern Poland. *Air and Soil Pollution* **216,** 217-228

Tyson, R.V. (2001) Sedimentation rate, dilution, preservation and total organic carbon: some results of a modelling study. *Organic Geochemistry* **32,** 333-339

Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., (2001) Mercury in the aquatic environment: A review of factors affecting methylation. *Critical Reviews in Environmental Science and Technology* **31,** 241-293

Vale, C., Catarini, F.M., Cortesao, C. and Cacador, M.I. (1990) Presence of metal-rich rhizoconcretions on the roots of Spartina maritime from the saltmarshes of the Tagus estuary, Portugal. *Science of the Total Environment* **97/98**, 617-626

Valette-Silver, N.J. (1993) The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediments. *Estuaries* **16**, 577-588.

Van der Post, K.D., Oldfield, F., Howarth, E.Y., Crooks, P.R.J. and Appleby, P.G. (1997) A record of accelerated erosion in the recent sediments of Blelham Tarn in the English Lake District. *Journal of Paleolimnology* **18**, 103-120

Van den Berg, M., Birnbaum, L., Bosveld, A.T.C., *et al.* (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives* **106,** 775

Van Dort, H.M., Smullen, L.A., May, R.J. and Bedard, D.L. (1997) Priming meta-dechlorination of polychlorinated biphenyls that have persisted in Housatonic river sediments for decades. *Environmental Science and Technology* **31**, 3300-3307

Van Metre, P.C., Mahler, B.J. (2003) The contribution of particles washed from rooftops to contaminant loading to urban streams. *Chemosphere* **52,** 1727-1741

Vane, C.H., Harrison, I., Kim, A.W. (2007) Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, UK. *Science of the Total Environment* **374,** 112-126

Vane, C.H., Jones, D.G., Lister, T.R. (2009) Mercury contamination in surface sediments and sediment cores of the Mersey Estuary, UK. *Marine Pollution Bulletin* **58,** 940-946

Velde, B., Church, T. and Bauer, A. (2003) Contrasting trace element geochemistry in two American and French saltmarshes. *Marine Chemistry* **83**, 131-144

Viguri, J., Verde, J., Irabien, A. (2002) Environmental assessment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Santander Bay, Northern Spain. *Chemosphere* **48,** 157-165

Vroom, F.Q., and Greer, M. (1972) Mercury vapour intoxication. *Brain* **95**, 305-318

Walter, H., Consolaro, F., Gramatica, P. *et al.* (2002) Mixture toxicity of priority pollutants at no observed effect concentrations (NOECs). *Ecotoxicology* **11,** 299-310

Warshawsky. D., Barkley. W., Bingham E. (1993) Factors affecting carcinogenic potential of mixtures. *Fundam Appl Toxicol* **20**, 376-382

Weber, J.H., Billing, M.R. and Falke, A.M. (1991) Seasonal methyltin and (3-dimeythlsulphonio)propionate concentrations in leaf tissue of *Spartina alterniflora* of the Great Bay estuary (NH). *Estuarine, Coastal and Shelf Science* **33**, 549-557

Webster, J.G. (1999). Arsenic. In: C.P. Marshall & R.W. Fairbridge (Eds.), Encyclopedia of geochemistry. Kluwer Academic Publishers, Dordrecht, Germany, 21-23.

Whatmore, T. (1990) My life at Speke Hall. Graphic Solutions Publications

Wheeler, A.J., Oldfield, F., Orford, J.D. (1999) Depositional and post-depositional controls on magnetic signals from saltmarshes on the north-west coast of Ireland. *Sedimentology* **46,** 545-558

Williams, T.M. (1993) Articulate metal speciation in surficial sediments from loch dee, southwest Scotland, UK. *Environmental Geology* **21**, 62-69

Witt, G. (2002) Occurrence and transport of polycyclic aromatic hydrocarbons in the water bodies of the Baltic Sea. *Marine Chemistry* **79,** 49-66

WHO, *Environmental Health Criteria 108: Nickel.* World Health Organisation, Geneva. 1991.

Williams, T.P., Bubb, J.M. and Lester, J.N. (1994) Metal accumulation within saltmarsh environments: a review. *Marine Pollution Bulletin* **28,** 277-290

Wilson, G.P., Lamb, A.L., Leng, M.J. *et al.* (2005) Variability of organic delta C-13 and C/N in the Mersey Estuary, UK and its implications for sea-level reconstruction studies. *Estuarine Coastal and Shelf Science* **64,** 685-698

Window, H., Schropp, S., Calder, F., Ryan, J., Smith, R., Burney, L., Lewis, F. and Rawlinson, C. (1989) Natural trace metal concentrations in estuarine and coastal marine sediments of the south eastern United States. *Environmental Science and Technology* **23,** 314-320

Worsley, A.T, Booth, C.A., Power, A.L. (2005) Atmospheric pollution and human health: the significance of a datable sedimentary archive from a small urban lake in Merseyside, UK. 3rd international conference on the impact of environmental factors on health, date: sep 14-16, 2005 bologna italy *Environmental Health Risk iiI* **9,** 199-208

Worsley, A. T., Power, A. L., Booth, C. A. (2006). Air pollution records from urban lake sediments: The implications of datable, lacustrine sedimentary archives for epidemiology. In J. W. S. Longhurst & C. A. Brebbia (Eds.), *Air pollution XIV* 735–744

Wright, P., Mason, C.F. (1999) Spatial and seasonal variation in the sediments and biota of two adjacent estuaries, the Orwell and the Stour, in eastern England. *The Science of the Total Environment* **226,** 139-156.

Yamamuro, M., Kayanne, H. (1995) Rapid direct determination of organic-carbon and nitrogen in carbonate-bearing sediments with a yanaco mt-5 chn analyzer. *Limnology and Oceanography* **40,** 1001-1005

Yamashita, N., Kannan, K., Imagawa, T. *et al.* (2000) Vertical profile of polychlorinated dibenzo-p-dioxins, dibenzofurans, naphthalenes, biphenyls, polycyclic aromatic hydrocarbons, and alkylphenols in a sediment core from Tokyo Bay, Japan. *Environmental Science & Technology* **34,** 3560-3567

Yang, H.D., He, B.Y., Cai, S.M. *et al.* (1997) Environmental implications of magnetic measurements on recent sediments from Lake Donghu, Wuhan. *Water Air and Soil Pollution* **98,** 187-195

Yang, H.D., Rose, N (2005) Trace element pollution records in some UK lake sediments, their history, influence factors and regional differences. *Environment International* **31,** 63-75

Yang, H.D., Rose, N.L., Battarbee, R.W. *et al.*(2002) Distribution of some trace metals in Lochnagar, a Scottish mountain lake ecosystem and its catchment. *Science of the Total Environment* **285,** 197-208

Yang, H.D., Rose, N.L., Battarbee, R.W., *et al.* (2002) Trace metal distribution in the sediments of the whole lake basin for Lochnagar, Scotland: a palaeolimnological assessment. *Hydrobiologia* **479,** 51-61

Yang, Y., Ligouis, B., Pies, C. *et al.* (2008) Occurrence of coal and coal-derived particle-bound polycyclic aromatic hydrocarbons (PAHs) in a river floodplain soil. *Environmental Pollution* **151**, 121-129

Young, L.B., Harvey, H.H. (1992) The relative importance of manganese and iron-oxides and organic-matter in the sorption of trace-metals by surficial lake-sediments. *Geochimica et Cosmochimica Acta* **56**, 1175-1186

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* **33**, 489-515

Zhang, W. Yu, L. and Hutchinson, S.M. (2001) Diagenesis of magnetic minerals in the intertidal sediments of the Yangtze estuary, China, and its environmental significance. *The Science of the Total Environment* **266**, 196-175

Zhang, W.G., Yu, L.Z., Lu, M, *et al.* (2007) Magnetic approach to normalizing heavy metal concentrations for particle size effects in intertidal sediments in the Yangtze Estuary, China. *Environmental Pollution* **147**, 238-244

Xia, X., Wang, R. (2008) Effect of sediment particle size on polycyclic aromatic hydrocarbon biodegradation: Importance of the sediment-water interface. *Environmental Toxicology and Chemistry* **27**, 119-125

Zwiernik, M.J., Quensen, J.F., Boyd, S.A. (1999) Residual petroleum in sediments reduces the bioavailability and rate of reductive dechlorination of aroclor 1242. *Environmental Science and Technology* **33**, 3574-3578

Zwolsmann, J.J.G., Berger, G.W. and van Eck, G.T.M. (1993) Sediment accumulation rates, historical input, post depositional mobility and retention of major elements and trace elements in saltmarsh sediments of the Scheldt estuary, SW Netherlands. *Marine Chemistry* **44**, 73-74